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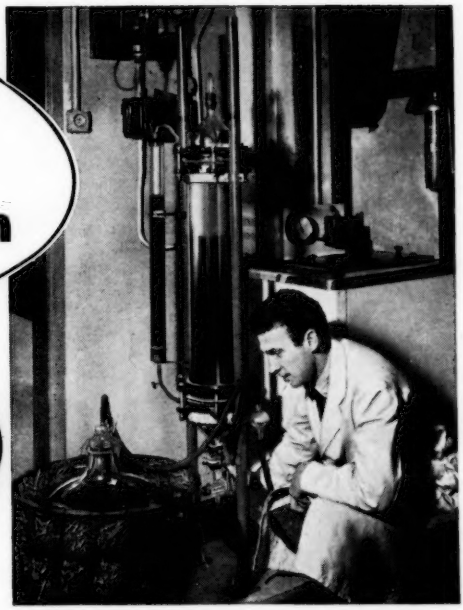

"Stilbazo" represents another flight of the chemist's fancy in the realms of abbreviated nomenclature. It stands for *di*-Ammonium stilbene-4 : 4′-*bis*-(1-azo-3 : 4-dihydroxybenzene)-2 : 2′-disulphonate. It can be identified also with equal brevity as H & W Code 9275.7 and is yet another reagent for aluminium.

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

253. **Further tests on the stability of analytical weights in chemical laboratories.** P. H. Bigg and F. H. Burch (*Brit. J. Appl. Phys.*, 1954, **5** [11], 382–386).—The stability of brass weights, coated electrolytically with nominal thicknesses of 13 μ and 25 μ of Sn - Ni alloy (65 per cent. of Sn), in the corrosive atmospheres of chemical laboratories has been investigated, and the corrosion is compared with that suffered by weights of other materials. After exposure, the 25-μ coated weight had the best appearance; corrosion was no more than with weights of highly polished stainless steel, except under the most severe conditions. These coated brass weights show about the same stability of mass as good-quality commercially produced weights of austenitic stainless steel (25 per cent. of Cr, 20 per cent. of Ni) and rhodium-plated brass weights. Weights plated with Ni - Sn have no undesirable magnetic properties. In highly corrosive atmospheres non-magnetic Ni - Cr (80 per cent. of Ni, 20 per cent. of Cr) weights are a little less resistant than the materials mentioned above. For the small sheet-metal weights the best material was austenitic stainless steel, followed (in order of merit) by Zr, Ta, Al and Ti. A. J. MEE

254. **Universal reagent for cleaning glassware.** R. H. A. Crawley (*Lab. Practice*, 1954, **3** [11], 462).—A wide variety of deposits may be moved effectively from glassware on treatment with a solution containing 5 per cent. of HF, 33 per cent. of HNO_3, 2 per cent. of Teepol and 60 per cent. of H_2O. Owing to slight attack on the glass, use of the solution with calibrated glassware is inadvisable. G. SKIRROW

255. **Sensitivity: a criterion for the comparison of methods of test.** J. Mandel and R. D. Stiehler (*J. Res. Nat. Bur. Stand.*, 1954, **53** [3], 155–159).—The criteria precision and accuracy are insufficient for the evaluation of many methods of test. Unless comparisons with a standard can be made, accuracy has no meaning. Precision, regarded as degree of reproducibility, is not necessarily a measure of merit, since a method may be highly reproducible merely because it is too crude to detect small quantities. A general mathematical definition is proposed for the sensitivity concept which is defined by the relation $\psi_M = (dM/dQ)/\sigma_M$, where M is a measure of some property Q, and σ_M is its standard deviation. Unlike the standard deviation this expression is independent of the scale in which the measurement is expressed. N. E.

256. **The colloid error of indicators.** C. F. Hiskey and T. A. Downey (*J. Phys. Chem.*, 1954, **58** [10], 835–840).—When trimethyloctadecylammonium chloride is added to methyl orange solution, there is a shift of the absorption spectrum max. of the latter from 507 mμ (acid form) or from 426 mμ (basic form) to a new max. at 463 mμ. This effect is found over a pH range of 0 to 12 on the addition of a 10^{-6} to 10^{-3} *M* soln. of quaternary salt to a $2{\cdot}04 \times 10^{-5}$ *M* soln. of methyl orange. The spectral change can be interpreted quantitatively as being due to the formation of a complex between the detergent and the basic form of the dye, according to the equilibrium: $'A' + Q \rightleftharpoons BQ + H^+$, where 'A', Q and BQ are the acid form of dye, quaternary salt and complex, respectively. The p*K* for this reaction is $-2{\cdot}41$, which means that the pK_a of methyl orange has been decreased by 6·2 units. Alternatively, the removal of the basic form of the dye may be due to its extraction from aq. soln. to a micellar oil phase. When the solubility of the complex BQ is determined in the presence of increasing amounts of Q, no solubilisation occurs before $[Q] = 3 \times 10^{-4}$ *M*, which is taken to be the critical micelle concn. It is possible to detect the effect of as little as $\simeq 3 \times 10^{-6}$ *M* of Q by the spectral change induced, so that sub-micellar units are presumed to form at this low concn. Continuous variation in absorbance makes it difficult to decide at what point the critical micelle concn. is reached when methyl orange is the indicator used. J. H. WATON

257. **Sensitised Schiff's reagent as an acid - base indicator.** S. N. Bhattacharya and A. Ghose (*Anal. Chim. Acta*, 1954, **11** [4], 309–312).—The sensitised Schiff's reagent of Tobie (*Brit. Abstr. A II*, 1942, 279) is used as an indicator for the titration of strong acids (0·1 *N* to *N*) with standard NaOH or aq. NH_3 soln. A dull-red colour precedes the equivalence point, which is marked by a sharp rise in the colour intensity. W. C. JOHNSON

258. **Systematic examinations of the analytical use of diethyldithiocarbamate. I. The stability of sodium diethyldithiocarbamate and its extraction in relation to pH.** H. Bode (*Z. anal. Chem.*, 1954, **142** [6], 414–423).—By studying the absorption spectra, at different pH values, of solutions of of sodium diethyldithiocarbamate (**I**), the decomposition is found to be a first-order reaction and is proportional to the hydrogen-ion concentration. It is recommended that the reagent be used at pH values > 6. Tetramethylenedithiocarbamate is found to be more stable, having a half-life of 69 min. at pH 2·4. The distribution coefficient between CCl_4 and water is proportional to the pH value. At pH > 8·5 negligibly small amounts of **I** go into the solvent phase. P. S. STROSS

259. **Structure and behaviour of organic analytical reagents. VII. Stability of chelates of 2-(o-hydroxyphenyl)benziminazole and analogous reagents.** W. D. Johnston and H. Freiser (*Anal. Chim. Acta*, 1954, **11** [4], 301–308).—The stability constants of some metal chelates of 2-(*o*-hydroxyphenyl)-pyridine, 2-(*o*-hydroxyphenyl)quinoline, 1-(*o*-hydroxyphenyl)*iso*quinoline, 2-(*o*-hydroxyphenyl)-benziminazole and 2-(*o*-hydroxyphenyl)iminazoline

have been determined by methods previously described (*J. Amer. Chem. Soc.*, 1952, **74**, 1383). The results are interpreted in terms of steric considerations. W. C. JOHNSON

260. **Sodium metavanadate as volumetric reagent. II. Iodine monochloride method. (Indirect determinations.)** Balwant Singh and Ranjit Singh (*Anal. Chim. Acta*, 1954, **11** [5], 412–416).—Sodium metavanadate affords indirect volumetric methods for the determination of H_2O_2, PbO_2, MnO_2, SeO_2, $K_2S_2O_8$, $CuSO_4$, Na formate and Na_2S. Excesses of appropriate reagents are added to each of the substances, and the excess is titrated with 0·1 *N* $NaVO_3$. The reagents are the same as those used in *Anal. Abstr.*, 1954, **1**, 1749 [$K_2S_2O_8$ is treated with an excess of $Fe(NH_4)_2(SO_4)_2$]. The excess is titrated by the general procedure described in *Anal. Abstr.*, 1954, **1**, 1749. W. C. JOHNSON

261. **Studies in oxidation - reduction reactions. I. Oxidation with chloramine-B, iodine monochloride method.** Balwant Singh and Krishan Chander Sood (*Anal. Chim. Acta*, 1954, **11** [4], 313–316).—Chloramine-B, $C_6H_5{\cdot}SO_2{\cdot}N(Na)Cl$ (**I**), is used to titrate the following substances (the mol. equiv. of **I** is indicated where it differs from unity): KI, As_2O_3 (2 **I**), Sb_2O_3(2 **I**), Hg_2Cl_2, $SnCl_2$, KCNS (3 **I**), $FeSO_4$ ($\frac{1}{2}$ **I**), N_2H_4(2 **I**) and quinol.

Procedure—Mix the sample in a flask with 25 ml of H_2O, 20 ml of conc. HCl, 5 ml of 0·02 *M* ICl and 5 ml of $CHCl_3$. Titrate with 0·1 *N* **I** until the aq. layer becomes pale yellow, stopper the flask and shake it vigorously. Continue the titration with shaking until the $CHCl_3$ is pale yellow. The strength of HCl soln. must be kept between 4 *N* and 5 *N*. W. C. JOHNSON

262. **Solutions standardised *per se*.** E. M. Gálvez Laguarta (*Inf. Quim. Anal.*, 1954, **8** [5], 153–156).—The analytical use of saturated standard solutions, the concentrations of which are known from the solubility of the solute, is described. Suitable substances for acidimetric and alkalimetric standards are $Ca(OH)_2$ and borax, and boric and tartaric acids, respectively. L. A. O'NEILL

263. **New titration methods in pharmaceutical laboratories.** B. Schmitz (*Dtsch. ApothZtg.*, 1954, **94** [24], 532–535).—The uses of ethylenediaminetetra-acetic acid and its disodium salt in the estimation of Mg, Zn, Ca and Hg in pharmaceutical analysis are reviewed. (8 references). F. R. MUMFORD

264. **Quantitative chemical analysis by means of stagoscopy.** A. Solé (*Z. anal. Chem.*, 1954, **142** [6], 412–414).—The name is applied to a method of detecting the end-point of certain reactions by observation of the formation of crystals of excess of reagent on a microscope slide. The estimations of NaCl with silver acetate and cholesterol with digitonin are quoted as examples. P. S. STROSS

265. **Absorptiometric analysis.** J. Bombí Llopis (*Inf. Quim. Anal.*, 1954, **8** [5], 169–179).—This is a summary of the principles and methods of absorptiometric analysis. A procedure is given for the determination by known methods of Mn, Cr, V, Cu, Co, Ni and Mo in a ferrous alloy. L. A. O'NEILL

266. **The mechanism of the platinum indicator electrode in argentimetry.** P. L. Allen and A. Hickling (*Anal. Chim. Acta*, 1954, **11** [5], 467–474).—The known ability of a platinum electrode to respond to changes of Ag^+ concn. is investigated. The response depends upon previous treatment of the electrode and, when the treatment consists of cathodic polarisation, the potentiometric curve for the titration of 0·1 *N* NaCl with 0·1 *N* $AgNO_3$ is identical with that given by a silver electrode. It is shown by expt. that this behaviour is due to a layer of Ag being formed on the surface of the Pt by interaction with Ag^+ in soln. If the pre-treatment is oxidising in effect, the silver layer is not acquired until the Ag^+ concn. rises to a sufficiently high value, *i.e.*, towards the end-point of the titration. The relative potentials involved are discussed with respect to platinum and to gold electrodes, which behave similarly, and consideration is extended to KCN - $AgNO_3$ titrations and to carbon electrodes. W. C. JOHNSON

267. **Determination of potentiometric-titration inflexion point by the concentric-arcs method.** C. F. Tubbs (*Anal. Chem.*, 1954, **26** [10], 1670–1671).—A template is prepared by making concentric arcs on a sheet of semi-rigid transparent sheeting. The template is placed on the potentiometric curve where the downward curvature starts, and the arc which coincides at most points is fitted. A mark is made on the graph where the centre of the arc lies. The procedure is repeated where the upward curvature begins. The two marks are joined, and the point where the line intersects the curve is taken as the point of inflexion. The results compare favourably with those obtained by other methods, and have less variability than those obtained by the visual method. J. H. WATON

268. **Some evaluations of high-frequency titration.** J. L. Hall, J. A. Gibson, jun., H. O. Phillips and F. E. Critchfield (*Anal. Chem.*, 1954, **26** [10], 1539–1542).—The approx. equiv. circuit of a high-frequency cell is compared with that of a conventional conductance cell of the same dimensions. The change of the radio-frequency component of conductance at the terminals of the high-frequency cell, for a given change of conductance of the soln. inside, is less than the corresponding change for the other cell. Numerical comparison of two high-frequency and two low-frequency instruments are made over various concn. ranges. Favourable comparison between the two types of instrument is found for certain concn. ranges at selected frequencies, the high-frequency apparatus having its greatest sensitivity near zero concn. Advantages of high-frequency titration methods are convenience, ease of recording and absence of metallic electrodes in the soln. Two examples of a titration in non-aqueous media are given to illustrate the relative merits of a potentiometric, a conventional conductimetric and a high-frequency conductimetric method. J. H. WATON

269. **Conductimetric standardisation of solutions of common divalent metallic ions, using disodium salt of ethylenediaminetetra-acetic acid.** J. L. Hall, J. A. Gibson, jun., P. R. Wilkinson and H. O. Phillips (*Anal. Chem.*, 1954, **26** [9], 1484–1486).—Standard soln. of disodium ethylenediaminetetra-acetate (0·1001, 0·04724, 0·01001 and 0·001004 *M*) are titrated conductimetrically in carefully buffered (NaOH - acetic acid or 3 *M* aq. NH_3) soln. with Cu^{++}, Ni^{++}, Co^{++}, Pb^{++}, Zn^{++}, Mn^{++}, Cd^{++}, Fe^{++}, Mg^{++}, Sr^{++}, Ca^{++}, Ba^{++}, Hg^{++}, La^{+++} and Ce^{++++} (as nitrates, perchlorates, chlorides, sulphates or acetates) soln.

of approx. equivalent concn. Conductivity measurements are made within a few ml of the end-point, at which a plot of specific conductance *vs.* titration shows an abrupt change of direction. Maximum error is 0·2 per cent. D. A. PANTONY

270. **Modified one-dimensional paper chromatography.** N. C. Ganguli (*Naturwissenschaften*, 1954, **41** [12], 282).—Small horizontal slots (2·5 × 5 mm) are cut at 5-mm intervals along a line 7 cm from the end of a large sheet of filter-paper (56 × 45 cm). This produces 15 strips of 3-cm wide. The material is applied to the 5-mm paper bridges. Development produces a radial solvent flow with improved power of resolution. E. KAWERAU

271. **A new form of paper-strip chromatography for serial analyses.** W. Matthias (*Naturwissenschaften*, 1954, **41** [1], 17).—One end of a sheet of filter-paper (40 × 28 cm) is cut so that 10 wedge-shaped tongues are formed, each one narrowing to a width of 2 mm at the tip before widening again to form a strip 1 cm wide. The material is applied at the foot of the constriction and is forced through the 2-mm wide paper bridge by the developing solvent mixture. Resolving power is increased and ten simultaneous analyses can be made on one sheet. E. KAWERAU

272. **Study of solvents used in adsorption chromatography.** P. B. Moseley, A. L. LeRosen and J. K. Carlton (*Anal. Chem.*, 1954, **26** [10], 1563–1566).—Adsorptives chosen to represent several structural classes are chromatographed on silicic acid and calcium hydroxide columns with several solvents. It is confirmed that there is a lack of correlation between developing power and physical properties such as dielectric constant and dipole moment. Hydrogen bonding is considered to play a significant part in the high adsorption affinity of certain functional groups, such as ·OH, ·COOH, :CO and ·CHO, for both adsorptive and solvent. The elution of *o*-nitroaniline on silicic acid is studied with two- and three-component mixtures as solvents, in order to provide data on developing power. A light petroleum - dibutyl ether mixture shows an approx. linear relationship between R_F values and the percentage of dibutyl ether, and is recommended as a solvent of general applicability because of its wide range of developing power. J. H. WATON

273. **Small-scale filter-paper chromatography. A rapid two-dimensional procedure.** L. B. Rockland and J. C. Underwood (*Anal. Chem.*, 1954, **26** [10], 1557–1563).—Amino-acids and related compounds in $\simeq$ 0·1-μg amounts in 0·1 to 1·0 μl of soln. can be identified by two-dimensional chromatography on sheets of S. & S. 589 blue-ribbon filter-paper 5 in. square. A *tert.*-butanol - water - formic acid mixture is used as the first solvent, and a phenol - water - aq. NH_3 mixture as the second. The effect of temp. on the R_F values of certain amino-acids is followed over the range 5° to 40° C. A chart is given showing the position of spots from about 60 amino-acids, peptides, carbohydrates and related compounds. J. H. WATON

274. **Immobile phase in chromatography on silicic acid - Celite. Role of water in the mechanism of development.** L. M. Kay and K. N. Trueblood (*Anal. Chem.*, 1954, **26** [10], 1566–1572).—The adsorptive power of silicic acid increases with the water content when highly polar ternary developers such as acetic acid - acetone - ligroin are used. To investigate this unusual increase in adsorption, the behaviour of the developing solvents is studied on treated and untreated (hydrous) silicic acid columns. From the R_F values of the polar components of binary and ternary developers, the composition and the relative vol. of the fixed and mobile liquid phases are worked out. The relatively high and varying value of the immobile liquid phase on the untreated column is attributed to hydrogen bonds provided by the water present. The R_F values for adsorptives on an untreated silicic acid column can be quant. explained by partition between the mobile and immobile phases when highly-polar developers are used. Partition alone will not account for the R_F values obtained when less-polar solvents or pre-washed columns are used, and adsorption is considered to be of primary importance. J. H. WATON

275. **Infra-red identification in paper chromatography.** T. Y. Toribara and V. Di Stefano (*Anal. Chem.*, 1954, **26** [9], 1519–1521).—The small amounts of material required in paper chromatography are difficult to convert to samples for infra-red identification. The difficulty can be overcome by the dilution of organic material in solid KBr. The quantitative transference and uniform dispersion of samples is achieved by freeze-drying a solution of the material and KBr. This method has the advantage of giving particles of optimum size for the production of the most satisfactory infra-red records. An apparatus suitable for the freeze-drying is described. J. H. WATON

276. **Multiple spots on paper chromatograms.** C. H. Hassall and K. E. Magnus (*Experientia*, 1954, **10** [10], 425–426).—The development of several spots on the chromatogram of a pure substance may be due to the formation of a new molecular species under the conditions of chromatography, but it is not always possible to account for them in this way. When the antibiotic monamycin was chromatographed, a "ghost" spot remained at the origin; this was readily eluted with methanol and was not due to an impurity. Similar results were obtained with digitoxin and azobenzene; they are attributed to partial irreversible adsorption of the solute on a cellulose phase when the mobile solvent phase is absent. N. E.

277. **A variant of circular filter-paper chromatography.** K. Starke (*Dtsch. ApothZtg.*, 1954, **94** [45], 1097).—The procedure of Töppel (*Angew. Chem.*, 1954, **66**, 555), in which a soln. is applied by elution from a cellulose column to a filter-paper held in a desiccator, has the disadvantage that the paper sags and wrinkles when wet. This may be overcome by supporting the paper between glass plates. A. R. ROGERS

278. **Chromatography of gases and vapours. IV. Applications of the surface-potential detector.** J. H. Griffiths and C. S. G. Phillips (*J. Chem. Soc.*, 1954, 3446–3453).—If two dissimilar plates connected by a conductor are placed close together, and one is set into vibration, an e.m.f. is set up because of the p.d. between the plates. This e.m.f. changes if the surfaces of the plates are exposed to an adsorbable vapour. The change in potential can be measured. Two steel plates were used, the surface of one being coated with stearic acid or with octadecanol. The surface potentials developed when N, saturated with various vapours, was passed between the plates (with one plate vibrating) have been

measured, and the relationship between the surface potential and concn. has been investigated for a number of substances. The isotherms are all of the same type, approaching a limiting value for the surface-potential change at high concn. of vapour. The method can be used for gas chromatography, and, because of the sensitivity of the detector to low concn. of vapour, the scale of gas chromatography can be considerably reduced. Four p.p.m. of ethyl oxalate in N will give a signal of 7·5 mV. The chromatography of high-boiling substances on low (room)-temp. columns, filled with sand or small glass beads, has been followed by the method. The substances are displaced from these columns by N saturated with diethyl malonate at 0° C. The detector is often highly selective and can be used for displacement analysis, and also for the determination of latent heats and vapour pressures. Compared with the thermal conductivity detector for gas chromatography, its disadvantages are sluggishness, non-linearity of response and, in a few instances, irreversibility. A. J. MEE

279. **On the method of paper electrophoresis of Grassmann and Hannig.** J. Pieper and H. Molinski (*Klin. Wochschr.*, 1954, **32** [41–42], 985–988).—The influence of various factors on the accuracy of the paper-electrophoretic separation of proteins by the Grassmann and Hannig technique (*Brit. Abstr. C*, 1952, 554) has been investigated. Full details of findings relating to the amount of serum used, temperature, duration of electrophoresis, technique of drying and staining and the measurement of transparency are given. No sources of error of any significance were found. The results of analysis of normal serum are compared with those obtained by the Antweiler technique.
G. W. CAMBRIDGE

280. **Preparation of compounds for infra-red spectrometry.** M. Hacskaylo (*Anal. Chem.*, 1954, **26** [9], 1410–1412).—Material for infra-red spectrometry is deposited as a thin layer on a sodium chloride plate. For soluble compounds, an $\simeq$ 0·1 *M* solution is applied with a small brush to a sodium chloride plate heated to a temp. greater than the vaporisation temp. of the solvent, but less than the decomposition temp. of the compound. If the absorption spectra are not satisfactory, the resolution of the curves can be greatly improved if the thickness of the surface layer is reduced by scraping it with a blunt smooth instrument. For insoluble compounds, the material is ground with a liquid of low vaporisation temp. to a thin paste or slurry, and then applied to the heated sodium chloride plate. Excess of sample is removed, preferably with another sodium chloride plate. Samples prepared in this way give excellent qualitative results, as the curves exhibit low background, good resolution and no extraneous bands.
J. H. WATON

281. **Nuclear magnetic resonance spectroscopy.** J. N. Shoolery (*Anal. Chem.*, 1954, **26** [9], 1400–1403).—Possible quantitative applications of nuclear magnetic resonance spectroscopy are indicated, such as the analysis of fluorocarbons and moisture determination. In the field of high resolution spectroscopy, nuclear magnetic resonance enables organic groups to be identified, and also yields information on the electron distribution and molecular structure of organic compounds.
J. H. WATON

282. **Determination of density of small fragments.** W. Primak and P. Day (*Anal. Chem.*, 1954, **26** [9], 1515–1517).—The flotation method of Hutchison and Johnston (*J. Amer. Chem. Soc.*, 1940, **62**, 3165; *J. Chem. Phys.*, 1940, **8**, 869) is extended to particles in the range of 40 to 100 mesh. The precision, which is lower, is limited by the size of the particle, the viscosity of the flotation liquid, the heat diffusivity of the flotation chamber and the length of time of observation of the liquid. The control of temp. no longer limits the precision, and interference from convection currents is decreased by the smaller diameter of the flotation vessel. Results in accordance with the predictions are given for silicon carbide, boron carbide, diamond, spinel and corundum. J. H. WATON

283. **Simple air-permeability method for measuring surface areas of fine powders.** H. J. Kamack (*Anal. Chem.*, 1954, **26** [10], 1623–1630).—A simple and rapid manometric technique, based on the air-permeability method, is described for measuring the surface areas of powders. The technique is suitable for powders of average size 0·2 to 30 μ. The method is based on the slip-flow modification of the Kozeny - Carman theory. J. H. WATON

284. **Spectrophotometric study of some metal chelate complexes.** A. H. Wilkins (*Dissert. Abstr.*, 1954, **14** [6], 925).—New spectrophotometric reagents and procedures are described for determining Fe, Cu and Co, and additional data are provided for systematic predictions of the structure of reagents having improved properties. A series of substituted 2:2′-diquinolyls has been studied, and the most effective groups and positions of substituents previously described for 1:10-phenanthroline are found to be applicable also to 2:2′-diquinolyl. The dialkylaminoalkylamino derivatives of 1:10-phenanthroline are sensitive reagents for Fe and particularly suitable for use with a filter-type spectrophotometer. 2:9-Dimethyl-4:7-diphenyl-1:10-phenanthroline is the most sensitive specific reagent for Cu. A procedure for determination of Cu in steel is described. A new procedure has been developed for the simultaneous determination of Cu and Fe with 1:10-phenanthroline, the 1:10-phenanthroline - Cu^{I} complex being extracted from aq. solution. Two new terpyridine derivatives, terosole and terosine, are better reagents for Co than the unsubstituted terpyridine, whilst terosole is the most sensitive reagent yet proposed for Fe. A procedure for determination of Fe in presence of Co by use of terosine is described and a new compound, 2:6-bis-(4-phenylpyridine)-4-phenylpyridine (terosite), is suggested for the determination of Fe and Co.
L. F. TAYLOR

See also Abstract 522.

2.—INORGANIC ANALYSIS

285. **Determination of water by the Karl Fischer method.** British Standards Institution (B.S. 2511: 1954, 22 pp.).—For the highest degree of accuracy, a double-burette system involving an electrometric end-point is recommended; suitable apparatus is described in general terms. Single-burette systems that make use of either an electrometric or a visual end-point, are described for application when the highest accuracy is not required. Procedures for the preparation and standardisation of Fischer reagent and standard water soln. and for the determination of water in simple solid and liquid samples are given in detail. A. R. ROGERS

286. **Determination of the short-lived decay products of radon in natural waters.** P. K. Kuroda and Y. Yokoyama (*Anal. Chem.*, 1954, **26** [9], 1509–1511).—Fresh rain-water samples show an excess of decay products of Rn, having a radioactivity of half-life $\simeq$ 30 min. The Rn content of the water tested is $< 10^{-11}$ curie per litre, whilst the content of decay products varies from 5×10^{-9} to 60×10^{-9} curie per litre. In most spring waters there is a deficiency of short-lived decay products of Rn. When the Rn content of the water is $< 10^{-9}$ curie per litre, the decay products are estimated by co-precipitation with PbS. When the sample has stood for $\simeq$ 3 hr. to establish equilibrium between Rn and its short-lived decay products, the radioactivity of the PbS ppt. is proportional to the Rn content of the spring water. This method may be used for the determination of Rn in mineral waters. J. H. Waton

287. **The determination of small amounts of lithium.** C. F. Forster (*Analyst*, 1954, **79**, 629–635).—In the method described the separated dry alkali chlorides, free from ammonium salts, are extracted with dry *n*-propanol and, after removal of the solvent, the weighed residue is dissolved in a solvent mixture of hexamine, water and acetone, and a ferricyanide reagent (prep. described) is added. The ppt. formed is collected, washed with aq. acetone and weighed. Alternatively, the ppt. is dissolved in water and its absorption is measured in a Spekker absorptiometer, the concn. of Li being ascertained from a calibration graph prepared with standard LiCl soln. In a micro-modification for amounts of Li < 50 μg, the ppt. is separated and washed by means of a filter stick and dissolved in a little water and ethanol, and a leuco-malachite-green soln. (prep. described) is added. The optical density is then measured on the absorptiometer. The calibration graph is prepared with standard LiCl soln. treated similarly. Heavy metals interfere and must be removed by the usual procedure. Ca can be removed as oxalate and Mg (and Ca if preferred) by 8-hydroxyquinoline. Permissible limits are given for other alkali metals. The probable formula of the yellow Li - K - hexamine ferricyanide complex is indicated; 48·905 g contains 1 g of Li. A. O. Jones

288. **Determination of small concentrations of sodium.** P. Mazzamaro and G. Tatoian (*Anal. Chem.*, 1954, **26** [9], 1512–1513).—Small (lower limit 6×10^{-7} g-equiv. per litre) concn. of $Na^{\cdot}$ are determined photometrically in an air - propane flame, the light emission being converted into electrical energy, which is measured on a high-sensitivity galvanometer. Results are compared with standards. Examination of distilled water from four sources showed absence of $Na^{\cdot}$, but results suggest that dil. H_2SO_4 leaches Na from glass storage vessels. D. A. Pantony

289. **Systematic investigation of the accurate determination of sodium with the Zeiss flame photometer.** F. Hegemann, V. Caimann and H. Zoellner (*Ber. dtsch. keram. Ges.*, 1954, **31** [9], 315–320).—The accuracy of the standard instrument was improved from $\pm$ 2 to 3 per cent. to $\pm$ 0·5 per cent. by adopting the following refinements: (*i*) operating the acetylene burner at the max. on the gas pressure - light intensity curve, when the variation in pressure has the least effect, (*ii*) measuring the pressure drop at the atomiser more accurately, with a liquid manometer, by keeping the nozzle free from incrustation, so minimising the fall in level of the solution in the supply vessel by using a dish of large diameter (*e.g.*, 7·7 cm), (*iii*) using a light meter to select the part of the Méker burner flame that flickers least, and minimising errors due to self absorption in the flame by diluting the solution according to the Na content, (*iv*) replacing the interference filters by a Zeiss - Opton Glasmonochromator M4, (*v*) replacing the selenium cell by a secondary electron multiplier, (*vi*) working at the most sensitive middle portion of the calibration curve, and (*vii*) removing the interfering $Ca^{\cdot\cdot}$ (by pptn. with ammonium oxalate) instead of using a correction curve. J. A. Sugden

290. **Flame-photometric determination of small amounts of potassium, sodium and lithium in the presence of larger amounts of alkaline-earth metals.** W. Schuhknecht and H. Schinkel (*Z. anal. Chem.*, 1954, **143** [5], 321–330).—Quantitative flame-photometric determination of alkali metals in the presence of alkaline-earth metals is possible if $Al(NO_3)_3$ is added to the test solutions. The complete quenching of the alkaline-earth emission by Al salts is discussed, and is attributed to formation of stable less-volatile chemical compounds of low thermal conductivity. D. R. Glasson

291. **The photometric determination of copper with hydrobromic acid.** W. Nielsch and G. Böltz (*Z. anal. Chem.*, 1954, **142** [6], 427–432).—The range of the previously described method (*Anal. Abstr.*, 1954, **1**, 2341 and 2414) is extended by the use of different filters so that from 4 to 40 μg per ml can be estimated without changing cells or repeating any part of the determination. The Cu must be separated from any Fe as the latter interferes. The Cu colour is depressed by H_3PO_4; HF cannot be used as a complexing agent as it attacks the glass cells. P. S. Stross

292. **A new photometric determination of copper with nitrilotriacetic acid.** W. Nielsch and G. Böltz (*Z. anal. Chem.*, 1954, **142** [6], 406–412).—The coloured complex of copper and nitrilotriacetic acid (**I**) is studied for its suitability for colorimetric estimations. The absorption maximum lies at $\simeq$ 700 mμ in alkaline solutions and $\simeq$ 655 mμ in acid solutions; the extinction is independent of pH between 3·20 and 6·0, and 8·65 and 9·50, and of temperature between 16° and 29° C. Any acid may be used to dissolve the metal. Excess of **I** does not interfere. The extinction reaches a constant value immediately after addition of the reagent, and obeys Beer's law for 0·04 to 7·0 mg of Cu per ml. Buffer soln. prepared from K tetraborate, Na tartrate, ammonium acetate of NH_4Cl may be used. P. S. Stross

293. **Copper[-in-gasoline] analysis by flame photometry.** J. H. Jordan (*Petrol. Refin.*, 1954, **33** [3], 158).—The proposed method consists in extracting Cu from gasoline with dil. HCl and determining the copper content of the acid extract by the use of a flame photometer. Results are reproducible within $\pm$ 10 per cent. and agree well with those obtained by conventional chemical analysis, which takes twice as long. J. Inst. Petrol

294. **Determination of traces of copper in germanium by activation analysis.** G. Szekely (*Anal. Chem.*, 1954, **26** [9], 1500–1502).—Cubic samples (0·1 g) are cut from Ge ingots, then sealed in silica ampoules and bombarded for 72 hr. with 3

to 4×10^{14} neutrons per sq. cm per sec. The cubes are etched twice in 6 *M* KOH containing 10 per cent. H_2O_2 (9 ml) for 5 min., and then dissolved in aqua regia (10 ml) in the presence of 50 mg of inactive Cu. After evaporation to dryness, the residue is taken up in HCl (10 ml); NaBr (0·5 g), hydrazine sulphate (0·5 g) and water (15 ml) are added and the soln. is distilled to remove As. The residue (approx. 5 ml) is diluted to 80 ml and filtered, the filtrate is saturated with SO_2, the pH is adjusted to 5 with aq. NH_3 and the Cu^{II} is pptd. with *N* KCNS. After being boiled, the suspension is filtered and the $Cu_2(CNS)_2$ is dissolved in aq. NH_3 (10 ml), a little SO_2 is introduced into the soln., the pH is adjusted to 5 with HCl, and *N* KCNS (1 drop) is added. The ppt. of $Cu_2(CNS)_2$, when filtered off, is free of all other radioactive contaminants. Sixty mg of the $Cu_2(CNS)_2$ are dispersed in collodion and the radio count is taken normally. Comparison with standard ^{64}Cu gives the Cu concn. The lower limit of sensitivity is 10^{-4} μg of Cu by the described method. D. A. PANTONY

295. **Ascorbimetric determination of silver ions.** L. Erdey and L. Buzás (*Acta Chim. Acad. Sci. Hung.*, 1954, **4** [2–4], 195–209).—A direct reductimetric method for the determination of Ag^+, which can be carried out with an error of ± 0·01 per cent., depends on titration with 0·1 *N* ascorbic acid in neutral or slightly acid solution in the presence of Variamin blue indicator. A solution containing 25 to 250 mg of Ag^+ is diluted with water so that the final volume after titration is ≃ 100 ml. The solution is heated to 60° C, 0·1 to 0·5 ml of 1 per cent. Variamin blue is added and 0·1 *N* ascorbic acid soln. is run in until the blue colour disappears. A 20 per cent. w/v soln. of Na acetate is added until the blue colour reappears, and the titration is completed by adding further ascorbic acid soln. until the complete disappearance of the blue colour. The results agree well with those by the Volhard method. Substances giving a ppt. with Ag^+ interfere, as do strong oxidising and reducing agents. Methods are described for eliminating these interferences. N. E.

296. **Extraction of silver and copper by dithizone. Properties of the "keto" dithizonates of silver and copper.** B. Tremillon (*Bull. Soc. Chim. France*, 1954, [9], 1156–1160).—In a sufficiently acid medium the "keto" form of dithizone is present, but, as the pH and concn. of cation increase, a change to the "enol" form slowly occurs. From an investigation of the extraction of the "keto" dithizonates of Ag and Cu by CCl_4, the equilibrium constants k_1 and k_2 are determined and the formulae of the complexes formed for both metals are deduced. The behaviour of the Ag and Cu complexes are investigated spectrophotometrically, the former by the "isobestic bundle" method by using Ag^+ buffered solutions, and the latter by the methods of continuous variations and linear determination curves at different pH values.

The formulae of the "keto" dithizonates of Ag and Cu are given as AgHDz and $Cu(HDz)_2$, respectively, where Dz represents dithizonate. The equilibrium constant for Ag is $10^{7\cdot6} \pm 0\cdot15$ and for Cu $10^{10\cdot4} \pm 0\cdot3$.
R. J. MAGEE

297. **Extraction of silver and copper by dithizone. Properties of "enol" dithizonates of silver and copper and applications.** B. Tremillon (*Bull. Soc. Chim. France*, 1954, [9], 1160–1163).—By the procedure in abstract 296 above, the "enol" dithizonates of Ag and Cu are investigated. In an acid medium, pH < 3·5, and with a sufficient excess of cation (10-fold for Cu and 1000-fold for Ag, the "enol" forms are obtained, Cu slowly (some hours) and Ag rapidly (some minutes). The Cu complex is studied by the "isobestic bundle" method; it has the formula CuDz and an equilibrium constant $10^{-6\cdot0} \pm 0\cdot2$. The Ag complex is insoluble in CCl_4, but from a series of adsorption curves the formula is shown to be Ag_2Dz, and the equilibrium constant $10^{5\cdot7} \pm 0\cdot3$.
R. J. MAGEE

298. **Oxyquinolate [8-Quinolinoxide] determination of magnesium oxide in cement.** L. Bean and N. J. Tucker (*Bull. A.S.T.M.*, 1954, No. 201, 62).—A simple modification saves 1½ to 2 hr., without loss of accuracy, when determining MgO by the A.S.T.M. alternate method (titration of Mg 8-quinolinoxide). When a determination of Ca is not required, the Ca oxalate can be pptd. in a vol. of 300 ml, and the soln. plus ppt. can be digested for 15 min. (water-bath) instead of remaining for 1 hr. at room temp. and being reheated to 70° C before the addition of 8-hydroxyquinoline. W. J. BAKER

299. **A simple micro-titration method for the determination of calcium and magnesium in the haemolymph of insects.** K. van Asperen and I. van Esch (*Nature*, 1954, **174**, 927).—The haemolymph (5 to 20 μl) is diluted immediately after collection with 100 μl of H_2O. The pH is adjusted and the soln. is titrated with ethylenediaminetetra-acetate by the Linderstrøm - Lang method. The concn. of Ca is found with murexide as indicator, and the total Ca plus Mg with Eriochrome black T. Calcium values agree with those obtained by other workers. Differences in values for Mg may be due to the dry-ashing procedures used by other workers.
C. E. SEARLE

300. **Coulometric titration of zinc with ferrocyanide.** J. J. Lingane and A. M. Hartley (*Anal. Chim. Acta*, 1954, **11** [5], 475–481).—Zinc is titrated with ferrocyanide generated at constant current by the reduction of ferricyanide at a platinum electrode. The supporting electrolyte is 0·2 *M* $K_3Fe(CN)_6$ adjusted to pH 2·0 ± 0·1 with HCl; Zn is pptd. from this soln. as $K_2Zn_3[Fe(CN)_6]_2$. A preliminary titration with a small quantity of Zn^{++} is conducted to eliminate the effect of zinc-reactive impurities in the $K_3Fe(CN)_6$. The end-points in this and in the main titration are taken at a potential slightly above the equiv. point potential, which is + 0·58 V *vs.* the S.C.E. at pH 2·0. Quantities of Zn from 3 to 30 mg are titrated at 3 to 94 mA in 100 to 600 sec., with an average error < ± 1 per cent.
W. C. JOHNSON

301. **Thermolysis of zinc monosalicylaldoxime.** J. Rynasiewicz and J. F. Flagg (*Anal. Chem.*, 1954 **26** [9], 1506).—Zinc monosalicylaldoxime is pptd. with various amounts of reagents, and the ppt. have been examined thermo-analytically. From the graphs of weight plotted against temp. it is concluded that the ideal drying temp. is 110° C and that an excess of 20 per cent. of salicylaldoxime should be used in the pptn., when an almost stoicheiometric complex results. ZnO is produced quantitatively between 500° and 1000° C.
D. A. PANTONY

302. **Polarographic determination of zinc in gold.** S. B. Deal (*Anal. Chem.*, 1954, **26** [9], 1459–1460).—The sample (1 g) of Au - Zn alloy containing 0·001 to 1 per cent. of Zn is dissolved in aqua regia (20 ml) and the soln. is evaporated cautiously to dryness.

The residue is dissolved in approx. 50 ml of warm water and conc. HCl (1 ml) is added. Gold is pptd. by the addition of saturated aq. SO_2 (25 ml) and digestion at 100° C for 1 hr., a further 10 ml being added at the end of this period, the digestion being extended for 10 min. After being cooled, the suspension is made up to 100 ml; 50 ml of this soln. are made up to 100 ml with 4 *M* aq. NH_3 - 4 *M* NH_4Cl soln., and a portion of the resulting soln. is examined polarographically over the range 0·9 to 1·65 V. Zn is determined from calibration curves. Analyses of 6 synthetic Zn - Au samples are given.

D. A. PANTONY

303. **The separation of zinc from other elements by the use of activated copper.** A. Bryson and S. Lenzer-Lowy (*Analyst*, 1954, **79**, 636–640).—Zn can be separated from other metals by the addition of activated copper powder to a soln. containing KCN and tartrate. The sample (containing $\not>$ 200 mg of Zn) is dissolved in aqua regia, fumed with H_2SO_4 and the diluted soln. is boiled with Na K tartrate. The cooled soln. is neutralised with solid Na_2CO_3; KCN (10 times the wt. of the metal) is added and then freshly prepared Cu powder (Bryson *et al.*, *Brit. Abstr. C*, 1953, 340) is added gradually to the soln., which is kept boiling, until the red colour persists. The ppt. (Pb, Bi, Sn, Cd, Ag and Hg) is removed by filtration, the filtrate (containing Zn, Co, Ni, Cu, Fe and Al) is made alkaline with NaOH and the Zn is pptd. with Na_2S. The ZnS is collected on filter-paper, washed with NaCl soln., and dissolved in dil. acid, and the Zn is determined gravimetrically or volumetrically. Mn must be removed before adding the copper powder.

A. O. JONES

304. **Decay and growth tables for the naturally occurring radioactive series: correction.** H. W. Kirby (*Anal. Chem.*, 1954, **26** [9], 1513).—Several significant errors in four of the tables of a previously published paper (*Anal. Abstr.*, 1954, **1**, 2331) are corrected.

D. A. PANTONY

305. **Separations of radio-elements by ion exchange.** P. Radhakrishna (*J. Chim. Phys.*, 1954, **51** [7–8], 354–357).—^{223}Ra (AcX) and ^{222}Ac(meso-Th II) are each separated from ^{234}Th(UX_1) by ion-exchange resin Dowex 50 at temp. $\simeq$ 80° C. About 70 per cent. pure UX_1 and 85 per cent. slightly impure AcX are obtained on elution with 7 per cent. oxalic acid soln. and 3 *N* HCl soln. Samples of UX_1 and meso-Th II of 95 per cent. purity are eluted with 7 per cent. oxalic acid soln. and 5 per cent. citric acid soln. (pH 3). ^{210}Bi (RaE) and Po are separated in 91 per cent. purity at room temp. by means of Dowex 50 resin with 2 *N* HNO_3 and 2 *N* HCl.

D. R. GLASSON

306. **Colorimetric determination of boron with tetrabromochrysazin.** J. H. Yoe and R. L. Grob (*Anal. Chem.*, 1954, **26** [9], 1465–1468).—A soln. containing 2·5 to 8·5 μg of B is distilled completely in the presence of methanol (25 ml), the distillate being collected under ice-cooled 0·1 *N* NaOH (5 ml). The resulting soln. is evaporated to dryness and to the residue is added the reagent (0·0556 per cent. of tetrabromochrysazin in 96 per cent. H_2SO_4) (1 ml). After 1 hr., the vol. is made up to 10 ml with 96 per cent. H_2SO_4 and the absorption is measured at 540 mμ against a reagent blank. The boron concn. is derived from standards. Tolerance limits of 22 ions are given, and if these are not exceeded, the distillation with methanol may be avoided. Standard deviation is given as 0·04 per cent. at a maximum recovery of 98·35 per cent. of B. Dilution limit is given as 1 in 5×10^7 for qualitative tests. The effect of H_2SO_4 concn. is examined, and the B to tetrabromochrysazin molecular ratio is established as 1 to 1.

D. A. PANTONY

307. **Simple determination of boron in plants by 1:1′-dianthrimide.** H. Baron (*Z. anal. Chem.*, 1954, **143** [5], 339–349).—Small amounts of boric acid are determined colorimetrically to an accuracy within $\pm$ 2 per cent. by means of the blue compound formed with 1:1′-dianthrimide (1:1′-dianthraquinonylamine) in conc. H_2SO_4. The max. sensitivity is given with 2·5 ml of aq. test solution to 17·5 ml of H_2SO_4, the blue colour completely developing in 5 hr. at 70° C.

D. R. GLASSON

308. **Studies on the reaction aluminium - morin. I. A new method for the colorimetric determination of aluminium ions.** Z. G. Szabó and M. T. Beck (*Acta Chim. Acad. Sci. Hung.*, 1954, **4** [2–4], 211–222).—The fluorescence and absorption spectra of the Al - morin complex have been established, and the effects of different factors (temp., alcohol, etc.) on the extinction values, fluorescence and turbidity have been examined. Colorimetric determination in a medium of 96 per cent. ethanol can be carried out easily and accurately. The ratio of Al to morin in the complex is 1 to 1 and not 1 to 3 as assumed by Schantl (*Mikrochem.*, 1924, **2**, 174). The substance to be analysed is dissolved in ethanol and, after separation by chromatography, is eluted with ethanol; the eluate is transferred to a 25-ml calibrated flask, 5 ml of 3×10^{-4} *M* per litre soln. of morin in ethanol is added, and the vol. is made up to 25 ml with ethanol. The colour is measured in a colorimeter, a S 42 filter being used, with a 6×10^{-5} *M* soln. of morin in ethanol to compensate for the colour of the reagent.

N. E.

309. **Complexometric titrations (chelatometry). V. Masking of aluminium and iron in titrations using Eriochrome black T as indicator.** R. Přibil (*Coll. Czech Chem. Comm.*, 1954, **19** [3], 465–469).—In the complexometric determinations of Mg, Zn, Cd and Mn with Eriochrome black T as indicator, triethanolamine is used for masking Al. Low Fe^{III} concn., which interferes by oxidising the indicator, are masked by triethanolamine and KCN. Commercial triethanolamine can be used for determining Mg if the metallic impurities are complexed with KCN. [This is a translation into German of a paper originally published in *Chem. Listy*, 1954, **48**, 382.]

D. R. GLASSON

310. **Radiochemical determination of neodymium, praseodymium and cerium in fission products.** H. G. Petrow (*Anal. Chem.*, 1954, **26** [9], 1514–1515).—The U specimen is allowed to age for 9 days to allow decay of ^{143}Ce to ^{143}Pr and then dissolved in HNO_3; the soln. is made up to 250 ml in the presence of 10 mg of inert Nd and a ^{147}Pm carrier. To an aliquot are added 15 mg of Nd, Pr and Ce carriers and 30 mg of Zr····. The Nd, Pr and Ce isotopes are separated by standard methods, and the final soln., free from excess of acid, is made up to 5 ml and passed through a cation-exchange column (colloidal Dowex 50 prepared with 4·25 per cent. lactic acid). Elution is carried out with 4·25 per cent. lactic acid (pH 3·30). After $\simeq$ 320 ml of eluate have been collected, each 10-ml fraction is examined for Nd; after its first appearance, all the Nd is contained in the next 80 ml. After a further

20 ml, all the Pr appears in the next 90 ml. Pm, if present, passes through the column before the Nd. The rare earths are detected and determined by pptn. as oxalates and radio-counting of the oxalate ppt. Contamination of any fraction by any other is < 1 per cent. D. A. PANTONY

311. **Analysis of inorganic compounds by paper chromatography. VI. Further studies on the separation and detection of lanthanons.** F. H. Pollard, J. F. W. McOmie and H. M. Stevens (*J. Chem. Soc.*, 1954, 3435–3440).—Tests for distinguishing lanthanon groups from some individual lanthanons are given, 8-hydroxyquinoline being used as complexing and detecting agent. Antipyrine, *o*-aminophenol and some substituted quinolines and pyridines have also been tried as complex-forming reagents, but the best separations are obtained with oxine in a *n*-butanol - H_2O - acetic acid mixture. The separations appear to depend on differences in ionic radii, Y coming between Gd and Dy. Factors affecting the percentage yield of "didymium" (Pr plus Nd) from a mixture with Ce have been investigated; successful separations on cellulose columns between members of the Ce group and between this group and Y have been carried out. From the results of paper-strip and column experiments it is predicted that good separations would be obtained between La or Ce and Pr to Lu (including Y) and between Pr or Sm and Dy to Lu (including Y) provided that the correct conditions of column length, flow-rate and load are observed. A. J. MEE

312. **The polarography of [tervalent] thallium.** G. W. Smith and F. Nelson (*J. Amer. Chem. Soc.*, 1954, **76** [18], 4714–4716).—Polarograms of Tl^{III} in chloride soln. are described and experimental values for diffusion current const. and diffusion coeff. are given. A method of using the polarograms for analysis of Tl^{III} and Tl^{I} mixtures is also described. H. F. W. KIRKPATRICK

313. **A simple and rapid method for the determination of carbon monoxide in air.** Yrjö Kauko and Muharrem Içel (*Z. anal. Chem.*, 1954, **142** [6], 401–406).—Air, or the gas containing carbon monoxide, is passed over iodine pentoxide or a mixture of MnO_2 (60 per cent.) and Cu_2O (40 per cent.). The CO is oxidised to CO_2, which is passed through absorption tubes containing a solution of $NaHCO_3$ (2×10^{-4} mole per litre) and KCl (0·0998 mole per litre). Quinhydrone is added, and the potential difference (E) between the test solution and a similar solution saturated with CO_2 is measured. The concentration of the gas is calculated as a percentage from the formula: $\log \frac{x}{100} = \frac{E}{0{\cdot}059} + 0{\cdot}15$. An alternative colorimetric method is described in which the pH difference is measured with bromothymol blue. P. S. STROSS

314. **Quantitative collection and recovery of silica by means of an ion-exchange column.** E. G. Brown and T. J. Hayes (*Mikrochim. Acta*, 1954, [5], 522–531).—The collection and recovery of SiO_2 on Amberlite IRA-400, a strongly basic anion-exchange resin, is described. The method is quantitative for amounts of SiO_2 between 40 and 200 μg. The method is applicable to metasilicate and fluorosilicate solutions. It was used successfully to determine traces of SiO_2 in Na alginate solutions, but failed in the separation of SiO_2 from NaOH solutions containing hemicellulose because some of the components of the latter were retained on the resin and were eluted afterwards by NaOH solution together with the SiO_2. A. J. MEE

315. **X-ray analysis of foundry dusts for quartz and iron in relation to silicosis and siderosis. I. Diffraction analysis for silica.** G. L. Clark, W. F. Loranger and S. J. Bodnar (*Anal. Chem.*, 1954, **26** [9], 1413–1416).—Standard dust samples are prepared containing known amounts of α-quartz mixed with silica, and with 20 per cent. of CaF_2 added as an internal standard. The X-ray diffractometer can then be calibrated by plotting percentage of quartz against the corrected intensity ratios of the 3·35 A line of quartz to the 3·16 A line of CaF_2, when a linear graph is obtained. For standard samples in the region 10 to 90 per cent. quartz, the method gives results with < 2 per cent. error. Before examining foundry dust samples, CaF_2 is added as an internal standard, but no diluent is necessary. J. H. WATON

316. **Quantitative analysis by X-ray diffraction. Determination of the various forms of silica.** A. Libertia and G. Collotti (*Ann. Chim., Roma*, 1954, **44** [7–8], 454–463).—By using fluorite as an internal standard, quartz, cristobalite and tridymite can be determined separately in minerals; the intensities of their X-ray diffraction at the angles for maximum reflection are measured with a Geiger-counter X-ray spectrometer, with an error of ± 5 per cent. R. C. MURRAY

317. **The determination of metallic lead in pigments.** A. Wooller (*Analyst*, 1954, **79**, 649–650).—In the volumetric method described, the principle of assaying Al powder by reduction of $Fe_2(SO_4)_3$ is extended to the determination of finely divided Pb in pigments. The pigment (≡ 0·2 g of Pb) is heated at 90° to 95° C with a $Fe_2(SO_4)_3$ - HCl - H_3PO_4 mixed reagent (prep. described) for ½ to 2 hr. with exclusion of air. The liquid is then cooled, diluted and titrated with 0·1 *N* $KMnO_4$. With Pb - Pb_3O_4 mixtures, the sample is titrated with saturated Na acetate containing 1 per cent. of acetic acid; 0·1 *N* $Na_2S_2O_3$ (50 ml) is then added and the mixture is stirred until the Pb_3O_4 disappears. The liquid is then filtered and the excess of $Na_2S_2O_3$ in the combined filtrate and washings is determined. The residue on the filter (mainly Pb) is washed with acetone, dried and weighed and the Pb is determined as before. With Al - Pb mixtures, the sample is treated with the $Fe_2(SO_4)_3$ reagent at 60° to 70° C for 15 min. The insol. matter (including Pb) is collected and the Pb is determined as before. The filtrate is diluted and titrated with 0·1 *N* $KMnO_4$. With Pb - Zn mixtures, the sample (≡ 0·1 g of Zn) is treated with the $Fe_2(SO_4)_3$ reagent and 0·1 *N* $KMnO_4$ at 20° C for 10 min. The insol. matter is collected and the Pb is determined as before. The filtrate is titrated with either 0·1 *N* $KMnO_4$ or 0·1 *N* $FeSO_4$, whichever is necessary. The Zn must be free from Al, Fe and Mg. A. O. JONES

318. **Rapid determination of thorium in ores. II. Estimation of trace amounts of thorium in complex minerals and ores.** M. M. Tillu and V. T. Athavale (*Anal. Chim. Acta*, 1954, **11** [4], 324–328).—A method is presented for the determination of Th in ilmenite, samarskite, columbite - tantalite and other ores. It deals with Th contents down to 0·01 per cent., with an accuracy of 5 per cent., and takes 2 days. The sample (1 g) is brought into soln. by first fusing it with Na_2O_2. Zirconium

nitrate is added to the soln. to provide a carrier and the phosphates are pptd. The ppt. is evaporated with aq. HF to eliminate SiO_2 and to dissolve other substances that interfere. Lanthanum nitrate is added to provide a carrier for the pptn. of Th as fluoride. The ppt. is converted to nitrate and the Th is pptd. as iodate in the presence of oxalic acid. The iodate is separated, treated with dil. H_2SO_4 and KI, and the liberated I is titrated with 0·01 *N* $Na_2S_2O_3$. W. C. JOHNSON

319. **The oxinates of thorium and some cerite earths.** N. Eswaranarayana and Bh. S. V. Raghava Rao (*Anal. Chim. Acta*, 1954, **11** [4], 339–349).—The acidity conditions for (*a*) initial and (*b*) complete precipitation of Th, Ce and La with 8-hydroxyquinoline (**I**) have been determined as follows: Th, (*a*) pH 3·5; (*b*) pH 3·85; Ce, (*a*) pH 4·4, (*b*) 5·55; La, (*a*) pH 4·8, (*b*) pH 5·75. Thorium is separated from Ce and La by pptn. with **I** at pH 3·9, but at pH 4·1 a double pptn. is necessary. In the determination of Th in monazite a double pptn. at pH 3·9 is required. The orange or red complex $Th(C_9H_6ON)_5$, which is pptd. at temp. $< 70°$ C, is shown by spectrophotometric examination to be a distinct compound and not a mol. addition compound of **I** with $Th(C_9H_6ON)_4$ (**II**). **II** is the yellow complex that is pptd. at temp. $> 50°$ C; it can be estimated spectrophotometrically in amounts down to the equiv. of 2 μg of ThO_2 per ml in 0·1 *N* HCl at 320 mμ or in acetone at 330 mμ. W. C. JOHNSON

320. **Colorimetric determination of nitrogen in biological materials.** J. R. Polley (*Anal. Chem.*, 1954, **26** [9], 1523–1524).—The biological samples are digested with a mixture of K_2SO_4, $HgSO_4$ and H_2SO_4. Free Hg is removed by the addition of Zn dust and heating until the reaction ceases. Sodium hydroxide is added and the N content is determined colorimetrically with Nessler's reagent on measuring the absorption at 450 mμ. Good precision is attained in the micro and macro ranges and an error of within $\pm$ 2 per cent. is obtained in the determination of N in amino-acids. The recovery of N from heterocyclic compounds is $>$ 94 per cent. Good recoveries are also attained from proteins. G. P. COOK

321. **The determination of phosphorus by the method of N. v. Lorenz (with a volumetric method by F. Scheffer).** Y. E. Stourdzé (Inst. Nac. Technol., Rio de Janeiro, 1953, 17 pp.).—The methods of Treadwell and v. Lorenz for the determination of phosphorus in phosphates and superphosphate of calcium and in iron and manganese ores, etc., have been compared, the latter method being modified by applying the volumetric method of F. Scheffer in which the pptd. molybdophosphate is dissolved in an excess of standard acid and titrated with alkali after the addition of formaldehyde. Agreement between Scheffer's titrimetric modification of v. Lorenz's method and weighing the pptd. P as $Mg_2P_2O_7$ was good. H. PRITCHARD

322. **Determination of phosphorus and arsenic (as phosphates and arsenates) by means of radioactive silver.** C. Barcia Goyanes, E. Sanchez Serrano and C. Gomis (*Bol. Radiactiv.*, 1954, **26**, 37–43).—The method of Spacu and Dima (*Z. anal. Chem.*, 1940, **120**, 217), in which phosphorus and arsenic are pptd. as Ag_2TlPO_4 and Ag_2TlAsO_4, respectively, by the addition of Tl acetate and $AgNO_3$, has been modified by the use of $AgNO_3$ labelled with ^{110}Ag. The activity of the ppt. is measured and related to the concentration by calibration curves. L. A. O'NEILL

323. **Application of absorption spectrum of sodium vanadate to determination of vanadium.** I. M. Gottlieb, J. F. Hazel and W. M. McNabb (*Anal. Chim. Acta*, 1954, **11** [4], 376–381).—In *M* NaOH, vanadate exists only as orthovanadate and such solutions exhibit an absorption max. at 270 mμ. This property is used in the determination of small quantities of V in rocks and minerals. Chromate and manganate also show absorption at 270 mμ and the method provides for the elimination of these radicles. *Procedure*—Fuse the sample (1 g) with Na_2CO_3 (5 to 6 g), heat the cake with water (5 to 10 ml) until decomposed, add methanol (3 to 5 ml) to reduce MnO_4'', heat to boiling, filter, wash the filter with hot water and dilute the filtrate and washings to 100 ml. To 10 to 20 ml, add methyl orange soln. and neutralise with 4 *N* H_2SO_4; add 8-hydroxyquinoline soln. [2·5 per cent. in dil. acetic acid (1 + 8), 2 to 3 drops] and extract with $CHCl_3$ (2 to 3-ml portions) until no more dark-coloured complex is formed with the $CHCl_3$. Evaporate the extracts with Na_2CO_3 (0·1 g) and then fuse the residue. Dissolve the melt in water (10 to 15 ml), add NaOH (4 g), filter if necessary and dilute with water to 100 ml. Measure the optical density at 270 mμ. Prepare a calibration curve (by using known amounts of V up to 12 μg per ml) as Na orthovanadate in *M* NaOH. W. C. JOHNSON

324. **Photometric determination of traces of antimony with rhodamine B after sulphide precipitation.** Hiroshi Onishi and E. B. Sandell (*Anal. Chim. Acta*, 1954, **11** [5], 444–450).—A method is presented for the determination of as little as a few tenths of a p.p.m. of Sb in mineral substances. Attention is given to the separation of Ga, Fe, Tl and Au; all of them give fairly sensitive colour reactions with rhodamine B. The Sb (0·5 to 2·5 μg) separated from elements of atomic numbers 1 to 28 by pptn. as Sb_2S_3 from a sulphuric - tartaric acid soln. The soln. also contains $CuSO_4$ to provide CuS as a collector; Fe^{III} is reduced with hydroxylamine before the sulphide pptn. After redissolving the ppt., the soln. is reduced with SO_2 and Ga is separated by extraction with di*iso*propyl ether from a soln. made 7 *N* in HCl. The soln. is then treated with ceric sulphate, followed by hydroxylamine, and H_3PO_4 is added to sequester any Fe that may have been co-precipitated with the sulphide. Rhodamine B soln. is added and the coloured antimony compound is extracted with benzene. The transmittancy of the extract is measured at 565 mμ and the Sb content is determined from a calibration curve. Up to 40 μg of thallium causes no error, but larger amounts should be separated by cupferron - $CHCl_3$ extraction (*Anal. Abstr.*, 1954, **1**, 907). Gold is filtered off after the SO_2 reduction. A large number of other metals were investigated; only V^V and W^{VI} interfered with the Sb - rhodamine B reaction, and V and W are not pptd. with H_2S from tartrate soln. W. C. JOHNSON

325. **Rapid method for the volumetric determination of antimony, copper or iron in textile materials.** A. G. Hamlin (*Shirley Inst. Mem.*, 1954, **27** [12], 195–203).—Organic matter is destroyed by wet-ashing with HNO_3, H_2SO_4 and $HClO_4$. If Sb is present, it is re-dissolved by boiling with HCl. The metals are reduced with $TiCl_2$ in hot dil. $HClO_4$

soln., the excess of reductant being oxidised on heating and estimated by oxidation with suitable reagents. When Sb is present, the oxidant used is $KBrO_3$; Cu is oxidised with ferric alum and Fe with ceric ammonium sulphate. The determinations of Sb and Cu or Sb and Fe in the presence of each other are described, but Cu and Fe cannot be determined separately. The method is subject to few interferences. A. M. SPRATT

326. **The photometric estimation of bismuth with hydrobromic acid.** W. Nielsch and G. Böltz (*Anal. Chim. Acta*, 1954, **11** [5], 438–443).—A soln. of $BiBr_3$ in conc. aq. HBr shows an absorption max. at 370 to 380 mμ; this characteristic can be used for the estimation of Bi. The extinction is independent of the HBr concn. between ≃ 20 and 48 per cent., but is depressed in the presence of HCl. Temp. variations between 15° and 30° C have no influence, and the extinction attains a constant value immediately. The Beer - Lambert law is obeyed for concn. of Bi up to 14 μg per ml; concn. up to 100 μg per ml can be determined by the use of a calibration curve. W. C. JOHNSON

327. **Rapid method for the separation and determination of bismuth, antimony and tin by controlled cathode electro-analysis.** J. A. Dean and S. A. Reynolds (*Anal. Chim. Acta*, 1954, **11** [4], 390–395).—Conditions have been investigated for the electrolytic separation of Bi, Sb and Sn, and the following method has been evolved. *Procedure*—Take a sample containing ≯ 0·1 g of Bi, ≯ 0·25 g of Sb and ≯ 0·25 g of Sn and dissolve it by heating with 10 ml of conc. H_2SO_4 and 0·5 g of hydrazine sulphate. Cool, dilute with 10 to 20 ml of water, add 30 ml of *M* Na citrate, 3 g of hydroxylamine or hydrazine sulphate and 10 *M* NaOH to make the pH ≃ 3. Cool, dil. to ≃ 130 ml and adjust to pH 3·0 (glass electrode). Heat to 79° to 80° C and deposit Bi on a platinum gauze electrode at −0·2 V (*vs.* the S.C.E.) increasing to −0·3 V, until the current falls to a small const. value. Wash the electrode with water and with acetone, dry and weigh the deposit and subtract 1·3 mg to obtain the wt. of Bi. To the electrolyte, add 1 g of hydrazine hydrochloride and 15 ml of conc. HCl and deposit Sb on a clean cathode at 50° to 70° C at ≯ 0·5 amp. and ≯ −0·3 V until the current falls to a small const. value. Deposit the Sn on a clean cathode at −0·6 V., increasing the potential to −0·65 V after 15 min.; syphon off the electrolyte while diluting with water (400 to 500 ml). Subtract 1·2 mg from the wt. of the deposit to obtain the wt. of Sn. Cu deposits with Bi, and Pb with Sn.
W. C. JOHNSON

328. **Improved techniques in the Unterzaucher oxygen determination.** L. J. Moelants and W. Wesenbeek (*Mikrochim. Acta*, 1954, [6], 738–742).—Suspected causes of high blanks in the Unterzaucher determination have been investigated. The quartz of the combustion tube and the carbon black must be of good quality and the temp. of the carbon contact furnace must be kept constant. High results are often caused by adsorption of air during flaming and cooling of the platinum sample boat. A method of purifying carbon black is described. The carbon is washed with ethanol and water; after filtration it is boiled with dil. HCl (1 + 1), the HCl is decanted and the residue is washed with water and ethanol. It is dried at 120° C and then heated for 8 hr. in nitrogen at 900° C. A. J. MEE

329. **Determination of oxygen by a (γ, n) reaction utilising a betatron.** R. Basile, J. Huré, P. Lévèque and C. Schuhl (*Compt. Rend.*, 1954, **239** [5], 422–424).—The proposed rapid direct estimation of O in organic compounds and in metals makes use of the reaction ^{16}O (γ, n) ^{15}O [half-life 118 sec., β^+ energy 1·7 MeV] initiated by betatron-generated X-rays of ≮ 15·5 MeV. Organic samples are irradiated for 4 min. at 20-cm distances by max. energy of 18·6 MeV, and metals at 40 cm by max. energy of 22 MeV. Calibration for organic samples is effected by means of pure sterol, stearic acid or benzoic acid; with bell counters, the sensitivity of detection of ^{15}O is 0·2 to 0·3 per cent. Measurements on metals are made in comparison with a standard sample of identical dimensions; sensitivity of detection of O (as Al_2O_3) in Al is ≃ 0·1 per cent. The method, which is non-destructive, can be extended to C and N in organic compounds, and its sensitivity can be increased by using an improved counter (*cf. Compt. Rend.*, 1953, **237**, 1696).
W. J. BAKER

330. **Improvements in the determination of small amounts of sulphur.** [**I and II.**] H. N. Wilson, R. M. Pearson and D. M. Fitzgerald (*J. Appl. Chem.*, 1954, **4** [9], 488–496).—**I.** A catalyst consisting of ceria on alumina is recommended for the determination of small quantities of S in preference to those previously described (*Brit. Abstr. C*, 1950, 399). The adsorption train of the apparatus has been improved. Commercial cerium oxide (30 g) is dissolved in nitric acid, diluted to ≃ 1000 ml with water and boiled. While hot, hydroxides are precipitated with aq. NH_3. After decanting, washing and reprecipitation, this ppt. is dissolved in a minimum of hot conc. acid. Activated alumina (270 g) is added and the mixture is evaporated to dryness with stirring; it is generally calcined to decompose the nitrate and break the mass up into granules. The mixture is finally calcined at 1300° C in air for 12 hr. **II.** A rapid volumetric method for determining low concn. of sulphate ion with disodium dihydrogen ethylenediaminetetra-acetate solution (EDTA) is described. The method gives results comparable with those obtained by the standard gravimetric procedure. The sample size is adjusted to give 1·0 to 20·0 mg and the contents and washings of the adsorbers are made up to 1000 ml with distilled water. A 500-ml portion is boiled and 50 ml of 0·02 *N* $BaCl_2$ are added. If the soln. is neutral to litmus, 10 ml of a buffer soln. are added and the mixture is titrated with 0·02 *N* EDTA to the first pure-blue end-point with the aid of an ethanolic solution of Solochrome black WDFA 150 as indicator.

Sulphur (g) in sample = {50 − (ml of EDTA)} × 0·00032 × 2.
D. LIFF

331. **The quantitative determination of small amounts of sulphur in biological material.** K. Tettweiler and W. Pilz (*Naturwissenschaften*, 1954, **41** [14], 332).—After oxidative digestion, sulphur is obtained as barium sulphate and the barium is determined by titration with the disodium salt of ethylenediaminetetra-acetic acid (**I**), with Eriochrome black T (Merck) as indicator. Since the Ba salt of Eriochrome black T does not change the colour of the indicator at the end-point of the titration, an additional complex-forming metal has to be used. A sharp end-point is obtained with the zinc complex of **I**. Barium quantitatively frees the zinc, and the zinc - Eriochrome black

complex can then be titrated with **I**. One drop of a 0·01 *M* soln. changes the ruby colour of the indicator to a pure blue. *Procedure*—To an aq. soln. containing sulphate equivalent to 0·01 to 5 mg of S in a vol. of 10 to 100 ml, add excess of 0·01 *M* $BaCl_2$, boil quickly and add 5 drops of 25 per cent. HCl. Cool to 40° to 60° C and add, for each 100 ml of soln., 1 g of solid NH_4Cl, 10 to 20 ml of conc. aq. NH_3 soln. and indicator. A knife-point of the zinc complex of **I** is added and the warm solution is titrated with **I**. The pptd. $BaSO_4$ makes recognition of the end-point particularly easy. The precision of a determination is ± 0·1 per cent. Foreign anions do not interfere; cations can be dealt with so that the titration can be carried out in the presence of ions of the heavy metals. With suitable modifications the method can be used for strontium and calcium. E. KAWERAU

332. **Polarographic determination of free sulphur in petroleum fractions.** S. Harrison and D. Harvey (*Analyst*, 1954, **79**, 640–643).—A method is described for the polarographic determination of free S in petroleum fractions, the solvent electrolyte medium being a 0·2 *M* soln. of ammonium acetate in glacial acetic acid. The petrol (5 ml) is made up to 25 ml with this solvent. A reduction wave of half-wave potential of −0·39 V is produced with a mercury-pool anode. The method is satisfactory for the direct determination of the free-S concn. from 0·5 to 10·0 p.p.m. Petrol with higher S content may be diluted with a standard petrol of known low S content. The presence of a large number of different organic S compounds gives no interference. A. O. JONES

333. **Titrimetric determination of sulphates by diazo titration of benzidine sulphate.** R. E. Keller and R. H. Munch (*Anal. Chem.*, 1954, **26** [9], 1518–1519).—The sulphate soln. is made just acid with a soln. of HCl and made up to approx. 100 ml with water and ethanol to bring the ethanol concn. to approx. 50 per cent. v/v. Benzidine dihydrochloride reagent [2 per cent. in dil. (1 + 250) HCl] is added in excess, slowly and with stirring; after 5 to 10 min., the ppt. is filtered off, washed and dissolved in water (10 ml) plus 6 *N* HCl (50 ml). A few crystals of KBr are added and the soln. is titrated potentiometrically (tungsten - calomel electrodes) with standard 0·1 *M* KNO_2, the end-point being detected by the largest voltage increase indicated on 0·1-ml additions of reagent. Maximum error varies from ± 3 to ± 0·8 per cent., depending on the SO_4'' concn. Organic sulphonates do not interfere, but PO_4''' (> 5 mg), CrO_4'' (> 10 mg), Cl' (> 500 mg) and Fe''' (> 10 mg as $FeCl_3$) affect the pptn., and hence the determination. D. A. PANTONY

334. **Cerimetric determination of mixtures of hydrogen peroxide, persulphuric acid (Caro's acid) and perdisulphuric acid.** L. J. Csányi and F. Solymosi (*Z. anal. Chem.*, 1954, **142** [6], 423–426).—To the solution to be analysed (60 to 70 ml), made *N* to 2 *N* with H_2SO_4, add a known excess of 0·1 *N* arsenite and titrate the H_2O_2 (**I**) with $Ce(SO_4)_2$, using ferroin as indicator. Add 0·01 *M* osmic acid (1 drop); the persulphuric acid (**II**) reacts with the arsenous acid, and the latter is then back-titrated with further $Ce(SO_4)_2$. To this solution, add conc. H_2SO_4 until the concentration is 18 to 20 per cent., add a further known excess of arsenous acid, heat to boiling for 6 to 8 min., cool to 30° to 40° C and back-titrate with $Ce(SO_4)_2$. The difference between the two titres is equivalent to the amount of perdisulphuric acid (**III**). During the last stages, air oxidation is prevented, *e.g.*, by adding marble chips. A slightly different technique is described which must be used if approximately equivalent proportions of **I**, **II** and **III** are present. Accuracy is 0·25 per cent., or, by potentiometric methods, 0·1 per cent. P. S. STROSS

335. **Formic acid as a reagent for alkaline permanganate. II. Potentiometric determination of quadrivalent selenium.** I. M. Issa, S. A. Eid and R. M. Issa (*Anal. Chim. Acta*, 1954, **11** [3], 275–282).—At 25° C and in a 1 to 3 *N* concn. of NaOH, Na_2SeO_3 (0·02 *N*) can be titrated potentiometrically with 0·1 *N* $KMnO_4$, which, under these conditions, is reduced to MnO_4''. Ten per cent. of NaCl is added to accelerate the reaction. At 90° C and in 0·1 *N* NaOH, Se^{IV} (0·004 to 0·1 *N*) can be titrated with 0·01 to 0·1 *N* $KMnO_4$, the latter being reduced to MnO_2. The reaction is accelerated by the addition of NaCl and $AuCl_3$. $KMnO_4$ (0·1 *N*) can be titrated with Na_2SeO_3 (0·1 *N*) in the presence of NaOH (0·5 to 3 *N*), but the error increases with weaker solutions and the addition of Ba'' is disadvantageous. Alternatively Se^{IV} (< 4 mg) is added to an excess of 0·01 to 0·1 *N* $KMnO_4$ in *N* NaOH, and, after equilibrium is attained, as indicated by the potential of a platinum electrode, the excess of $KMnO_4$ is titrated with Na formate or formic acid soln. (*Anal. Abstr.*, 1954, **1**, 2703). W. C. JOHNSON

336. **Colorimetric micro-determination of chromium and manganese in aqueous solutions.** Akiya Kozawa, Motoharu Tanaka and Kumazo Sasaki (*Bull. Chem. Soc. Japan*, 1954, **27** [6], 345–347).—Cr and Mn are co-precipitated with $Fe(OH)_3$. After redissolving the Cr and Mn, reduction of the soln. and addition of Al ions, the Cr is co-precipitated with Al, Mn remaining in solution with the bulk of the Fe''. *Procedure*—One litre of the aq. solution containing < 100 μg of both Cr and Mn is treated with a soln. containing 10 mg of Fe^{III} and neutralised with an excess of aq. NH_3 soln. at 30° to 40° C. After filtration, the ppt. of $Fe(OH)_3$ with Cr and Mn is dissolved in 10 ml of hot dil. H_2SO_4 (1 + 20). Ten mg of Al solution are added and 1 ml of 5 per cent. hydroxylamine sulphate. After being boiled, the solution is cooled and neutralised with aq. NH_3 (1 + 5), bromocresol purple being used as indicator. After a second pptn., the Cr is estimated colorimetrically with diphenylcarbazide and the Mn, in the joint filtrate, as permanganate. The method is accurate to within 2·5 per cent., but the use of an empirical curve is recommended for Cr. J. DAVIS

337. **Mercurous salts as new reductimetric reagents for titrations in alkaline medium. II. Titration of chromium salts, arsenites, hydrogen peroxide and hydrazine.** F. Burriel-Martí, F. Lucena-Conde and S. Arribas-Jimeno (*Anal. Chim. Acta*, 1954, **11** [3], 214–220).—The sample is oxidised with an excess of $K_3Fe(CN)_6$, which is titrated potentiometrically with 0·1 *N* mercurous perchlorate according to the procedure previously described (*Anal. Abstr.*, 1954, **1**, 1521). The method is applied to solutions of the substances that are ≃ 0·1 *N* in reducing power; 5 to 30-ml portions are taken for analysis. Chromic chloride soln. is treated with an excess (25 ml) of 4 *M* NaOH and oxidised to CrO_4'' with an excess of 0·1 *N* $K_3Fe(CN)_6$; 40 ml of *M* KI are added, and, after dilution to 100 ml with water, the soln. is titrated. Solutions of Na arsenite are

treated with excess of 0·1 *N* $K_3Fe(CN)_6$ and then with 25 ml of 4 *M* NaOH, heated to $\geq$ 90° C for 15 to 20 min. and cooled; water is added to make the final vol. 100 ml, followed by 40 ml of *M* KI, and the soln. is titrated. Hydrogen peroxide soln. is added to an excess of 0·1 *N* $K_3Fe(CN)_6$ previously mixed with 25 ml of 4 *M* NaOH; the soln. is heated to 70° to 80° C and shaken until gas evolution ceases. The following reaction takes place—

$$2[Fe(CN)_6]''' + H_2O_2 + 2OH' \longrightarrow 2[Fe(CN)_6]'''' + O_2 + 2H_2O.$$

The procedure is concluded as for arsenite. Hydrazine hydrate soln. is mixed with a 100 per cent. excess of 0·1 *N* $K_3Fe(CN)_6$ and then the same vol. of 2 *N* NaOH is added; the soln. is shaken and heated to 60° C. The following reaction takes place—

$$N_2H_4 + 4[Fe(CN)_6]''' + 4OH' \longrightarrow N_2 + 4[Fe(CN)_6]'''' + 4H_2O.$$

When the evolution of N ceases, the procedure is completed in the usual manner. W. C. JOHNSON

338. **Improvements in the absorptiometric determination of tungsten.** Methods of Analysis Committee, B.I.S.R.A. (*J. Iron and Steel Inst.*, 1954, **178** [3], 267–269).—The paper describes modifications to the absorptiometric method previously published (*Brit. Abstr. C*, 1953, 383). The solvent mixture has been modified to cater for higher tungsten contents. The amount of $TiCl_3$ soln. added is increased to 1·0 ml, thereby entirely suppressing interference from Mo. The sample is dissolved in an H_3PO_4 - H_2SO_4 mixture. After reduction with $SnCl_2$, the W is complexed with NH_4CNS soln. $TiCl_3$ is then added to complete the reduction and the resulting yellow colour is measured photometrically, the percentage of W being deduced from a previously prepared graph. The method is suitable for up to 3 per cent. of W, and the reproducibility at the 2 per cent. level is ± 0·05 per cent. of W. The interference caused by the ppt. produced by 2 per cent. or more of Cu can be reduced to negligible proportions by filtering through a dry paper into the absorptiometer cell. Vanadium interferes in all concentrations and a suitable correction must be applied. C. J. KEATTCH

339. **Separation and identification of tungsten, niobium and tantalum.** Reinaldo Vanossi (*An. Assoc. Quim. Argent.*, 1954, **42** [2], 59–89).—Tungsten, niobium and tantalum form thiocyanates that can be extracted from aq. soln. with ethyl acetate. The thiocyanates formed can be isolated sufficiently pure to enable specific identification. The sample is treated with acid and oxidised with Na_2O_2; a 5 *M* soln. of thiocyanate acidified with HCl, and sodium sulphite are then added. A volume of ethyl acetate, equal to the aqueous phase, is added to extract the thiocyanates. The extract is purified by washing with dil. HCl and further treated with thiocyanate. Niobium and tantalum are separated from tungsten by treating the residue with alkali when tungsten is dissolved. Identification of tungsten in the solution and the separation of tantalum in the form of a fluoride complex by means of ethyl acetate leaves niobium in the aqueous phase. Alternative treatments for the removal of interfering elements are given. H. PRITCHARD

340. **Direct colorimetric determination of small amounts of tungsten in titanium.** G. Norwitz and M. Codell (*Anal. Chim. Acta*, 1954, **11** [4], 359–366).—The method described depends upon the measurement of the yellow colour that CNS′ develops with a soln. containing W in a reduced condition. Bacon (Royal Aircraft Establishment Report No. Met 119) recommended $SnCl_2$ for the reduction, some Ti^{IV} remaining unreduced producing an interfering colour with CNS′; $SnCl_2$ also reacts with CNS′ to produce H_2S, which causes fading. Reduction with Zn overcomes these difficulties. The method is suitable for the determination of 0·005 to 0·3 per cent. of W in Ti. *Procedure*—Dissolve 0·2 g of the alloy by warming with 25 ml of conc. HCl soln. and 5 ml of water, cool and transfer to a 50-ml flask containing 0·7 g of granulated Zn (20 mesh). As soon as the reaction ceases, add 10 ml of aq. KCNS (5 per cent. w/v) and stopper the flask. After 15 min., dilute to 50 ml and measure the transmittance at 410 mμ. Prepare a calibration curve, using Ti sponge and known amounts of W.

Mo and V interfere. The effect of Cr is such that 1 per cent. of Cr ≡ 0·006 per cent. of W, and a correction can be applied. Cu must not exceed 0·2 per cent., Ni, 2 per cent and Co, 2 per cent.
W. C. JOHNSON

341. **Determination of uranium by reduction with stannous chloride.** A. R. Main (*Anal. Chem.*, 1954, **26** [9], 1507–1509).—A soln. of UO_2SO_4 (approx. 10 ml) is treated with iron (as a 0·2 *N* $FeCl_3$ catalyst soln.) (2 ml), conc. HCl (20 to 25 ml) and dil. (1 + 1) H_3PO_4 (4 ml). After heating to 96° to 99° C, a calculated excess of $Sn^{\cdot\cdot}$ [as 5 per cent. $SnCl_2.2H_2O$ in dil. (1 + 10) HCl] is added, and the heating is continued for 10 to 15 min. When cold, the excess of $Sn^{\cdot\cdot}$ is discharged with saturated $HgCl_2$ (20 ml), and 8 per cent. $FeCl_3$ (20 ml) is added. After dilution to 250 to 300 ml, the mixture is titrated with 0·02 *N* $K_2Cr_2O_7$, with barium diphenylaminesulphonate as indicator, in the presence of H_3PO_4 - H_2SO_4 mixture (1 + 3) (15 ml) and in an atmosphere of CO_2. When allowance is made for the indicator and catalyst blank, results are quantitative; average agreement within duplicates is ± 0·48 per cent. Arsenic, ClO_4', WO_4'', MnO_4', $NH_4^{\cdot}$, pyridine, BiO_3', $Co^{\cdot\cdot}$, SO_4'', Cl' and NO_3' (< 5 mg) do not interfere, but Mo^{VI}, $Cu^{\cdot\cdot}$, VO_4'''' and $Ti^{\cdot\cdot\cdot\cdot}$ lead to high results. Results on unknown samples agree closely with those from fluorimetric measurements. D. A. PANTONY

342. **Determination of uranium by means of alkali ferricyanides.** G. S. Deshmukh and M. K. Joshi (*Z. anal. Chem.*, 1954, **143** [5], 334–339).—The volumetric method described depends on quant. reduction of U to U^{IV} by Al and H_2SO_4, and subsequent oxidation to U^{VI} by an excess of alkali ferricyanide. The ferrocyanide produced is titrated with $Ce(SO_4)_2$, $Na_2S_2O_3$, H_3AsO_4 or $Na_2S_2O_3$ and H_3AsO_4. D. R. GLASSON

343. **Analysis of uranium in sea-water.** D. C. Stewart and W. C. Bentley (*Science*, 1954, **120**, 50–51).—U was extracted from the sample with 0·5 ml of 0·7 to 0·8 *M* dibutyl hydrogen phosphate in CCl_4 and transferred to a platinum counting plate, as was a subsequent wash of 0·5 ml of CCl_4; the CCl_4 soln. was evaporated to dryness and the plate heated in a flame. U was then determined by fission-fragment counting of the ^{235}U present, by placing in an Argonne heavy-water reactor. Average recovery of U was 94·5 per cent. Pacific Ocean water contained 2·49, Great Salt Lakes water 5·0 and local tap water 0·12 μg of U per litre.
H. F. W. KIRKPATRICK

344. **Polarographic behaviour of chlorides.** A. A. Vlček (*Coll. Czech. Chem. Comm.*, 1954, **19** [2], 221–233).—The probable primary process is the formation of a film of chlorine atoms which are adsorbed on the mercury surface; this is indicated by effects on the mean current of concn., drop-height, presence of gelatin, composition of the solution and measurement of the momentary current. This film later decomposes and with Hg_2^{++} produces Hg_2Cl_2, which forms a coherent layer on the electrode surface. Ionic species Hg_2Cl^+ and $Hg_2Cl_3^-$ are apparently present near the electrode. The magnitude of the current, i, is determined by the diffusion rate of Cl^- to the surface of the electrode, and the rate at which Hg_2^{++} are drawn through the adhering layer. The latter rate determines the value of i for higher chloride concn. The presence of gelatin at concn. of 0·05 per cent. stabilises the chloride step suitably for analytical purposes; this is demonstrated for the determination of chloride impurities in conc. KOH. [This is a translation into German of a paper originally published in *Chem. Listy*, 1953, **47**, 1598.]
D. R. GLASSON

345. **Formation of bromate in the oxidation of iodide by bromine.** P. W. Jenson and A. L. Crittenden (*Anal. Chem.*, 1954, **26** [8], 1373–1374).—Heim's suggestion as to the cause of unstable end-points in the U.S.P. XIII method of determining iodide in desiccated thyroid (*Brit. Abstr. C*, 1949, 239) is confirmed. Oxidation of I^- to IO_3^- must be done after acidification. B. J. W.

346. **Polarographic determination of bromides.** M. Hemala (*Chem. Listy*, 1953, **47** [9], 1323–1325).—The method is based on the oxidation of Br^- with NaOCl and on polarographic determination of the resultant BrO_3^-. Excess of NaOCl is destroyed by evaporation to dryness and ignition of the residue. In the presence of divalent cations (*e.g.*, Ca^{++}), $E_{\frac{1}{2}}$ of BrO_3^- is − 1·57 V and is sufficiently distinct from $E_{\frac{1}{2}}$ of IO_3^- (− 1·00 V). Excess of Cl^- and I^- can be present without interfering. *Procedure*—Mix the neutral or slightly basic sample (20 to 50 ml) with *M* NaOCl in 0·1 *M* NaOH (5 ml), evaporate to dryness and heat the residue at 200° C during 15 to 30 min. Cool, add 0·025 *M* HCl, some *M* $CaCl_2$ and a drop of 0·2 per cent. soln. of gelatin. Expel O with N and polarograph at 1·0 V. G. GLASER

347. **Comparison of incineration and chloric acid methods for the determination of chemical protein-bound iodine.** L. Zieve, M. Dahle and A. L. Schultz (*J. Lab. Clin. Med.*, 1954, **44** [3], 374–377).—A comparison is made between values for protein-bound iodine obtained by the alkaline-incineration method of Barker *et al.* (*J. Clin. Invest.*, 1951, **30**, 55) and the chloric acid method as modified by O'Neal and Simms (*Amer. J. Clin. Path.*, 1953, **23**, 493). No significant differences between values by the two methods were obtained on sera from 14 hypothyroid and 22 hyperthyroid patients, but the values on 50 euthyroid patients by the chloric acid method were significantly higher by $\simeq$ 1 to 1·5 μg per cent. Thus the use of the chloric acid method leads to a loss in discrimination between hyperthyroid and euthyroid patients. W. H. C. SHAW

348. **New photometric determination of iron with ethylenediaminetetra-acetic acid.** W. Nielsch and G. Böltz (*Mikrochim. Acta*, 1954, [5], 481–488).—Ferric compounds can be determined photometrically with complexone III. The yellow complex produced has an absorption max. below 366 mμ. For the same Fe^{III} concn. the extinction depends on pH value. It is constant over the pH ranges 0·80 to 2·80 and 3·92 to 5·10, so that either of these ranges may be satisfactorily used for the determination. The complex decomposes at pH > 10·5, when $Fe(OH)_3$ is pptd. The extinction coeff. does not depend on the acid radicles present. The Beer - Lambert law holds for concn. of 4 to 500 μg of Fe per ml. This method of determination is superior to many other photometric methods of determining Fe because weaker complex-formers do not interfere. A. J. MEE

349. **Masking of larger [>200-mg] amounts of iron in complexiметric titrations.** H. Flaschka and R. Püschel (*Z. anal. Chem.*, 1954, **143** [5], 330–334).—Methods of masking amounts of Fe < 200 mg in complexiметric titrations, with Eriochrome black T indicator, are briefly reviewed. Amounts of Fe > 200 mg are first reduced in weakly acid solution by ascorbic acid, which also reduces in alkaline solution in titrations with Eriochrome black T. The reduced solution is neutralised with aq. NH_3 soln. to a permanent turbidity, and KCN with NH_4Cl buffer is added; the formation of $K_4Fe(CN)_6$ is accelerated by heating to 70° to 80° C, when a clear liquid suitable for titration of Mg, Ca, Mn or Pb is obtained. D. R. GLASSON

350. **Study of the application of *iso*nitrosomalonyl-guanidine to the estimation of iron in aluminium alloys and zinc, and the estimation of cobalt in steel.** M. Jean (*Anal. Chim. Acta*, 1954, **11** [5], 451–462).—A blue colour, with an absorption max. at 630 mμ, results from the reaction of *iso*nitrosomalonyl-guanidine with Fe^{II} salts in slightly acid or alkaline soln. This reaction is applied to the estimation of Fe (up to 0·4 per cent.) in aluminium alloys. The Fe is reduced with hydroxylamine, and the addition of KCN prevents interference from Cu. The soln. is buffered at pH 6 and the optical density is determined at 630 mμ. A calibration curve is prepared with known amounts of Fe. For the estimation of ≯ 0·01 per cent. of Fe in Zn, the soln. is buffered at pH 6 to 6·5; for Fe contents down to 0·001 per cent., the soln. is buffered at pH 9 to obtain a more sensitive reaction. As zinc has an influence on the colour intensity, the calibration standards must contain an equiv. concn. of Zn. In the estimation of Co with the same reagent (*Brit. Abstr. C*, 1952, 299), the excess of reagent and the ferric complex can be destroyed with aq. Br instead of HNO_3.
W. C. JOHNSON

351. **Colorimetric determination of iron in titanium alloys.** G. Norwitz and M. Codell (*Anal. Chim. Acta*, 1954, **11** [4], 350–358).—Two methods are described for the determination of Fe in Ti alloys. Samples containing up to 0·75 per cent. of Fe can be analysed by the direct method when the following metals are present in more than the following percentages: Cr, 2; Mo, 1·6; V, 0·9; Ni, 1·2; Co, 1·0; W, 1·6. Larger amounts of these interfering metals are tolerated when the Fe content is > 0·75 per cent.; a smaller aliquot of the sample soln. is then taken. *Procedure* (*direct method*)—Dissolve 1 g of the alloy by heating it with 40 ml of dil. HCl (1 + 1) and dil. with water to 500 ml. For alloys containing up to 0·75 per cent. of Fe, take a 25-ml aliquot; for higher Fe contents take a proportionately smaller aliquot and dilute to 25 ml with dil. HCl (4 per cent. v/v). Add 10 ml of aq. hydroxylamine hydrochloride (2 per cent. w/v), 5 ml of aq. ammonium tartrate (10 per cent. w/v), 25 ml

of aq. Na acetate (10 per cent. w/v) and 10 ml of aq. *o*-phenanthroline (0·2 per cent. w/v); after 15 min. read the transmittance at 490 mμ. Prepare a standard curve by the same method, using refined titanium (Van Arkel) and known amounts of Fe.

When the ratio of interfering metals to Fe is large, the Fe is separated by extraction. *Procedure (ether-extraction method)*—Dissolve 1 g of the alloy, by heating it with 10 ml of water and 30 ml of conc. HCl, add Br until the blue titanous colour disappears, then boil for 10 min. Add 40 ml of dil. HCl (sp. gr. 1·10), cool to 10° C, extract with one 50-ml and four 30-ml portions of ether, and evaporate the extracts to dryness. Boil the residue with 30 ml of dil. (1 + 1) HCl, cool, dilute to 500 ml with water and proceed as in the direct method. If much Mo is present, boil the residue from the ether extract with 30 ml of dil. HCl (1 + 1) and 1 ml of conc. HNO_3, dilute with water to 100 ml, add aq. NH_3 soln. (sp. gr. 0·90) in excess and boil for 1 min. Filter, and wash the ppt. with hot aq. NH_3 soln. (3 per cent. v/v). Dissolve the ppt. in hot dil. HCl (1 + 1), dilute with water to 500 ml and proceed as in the direct method.

W. C. JOHNSON

352. **Manganese dioxide - asbestos in steel analysis.** A. P. Lunt (*Analyst*, 1954, **79**, 651).—The acid $AgNO_3$ soln., for absorption of S oxides in the combustion train for determining C in steels of high S content, can be replaced with advantage by a dry MnO_2 absorbant. Ignited asbestos fibre (25 g) is shaken with 400 ml of saturated $KMnO_4$ soln. in a 2-litre flask; a further 400 ml of saturated $MnSO_4$ are then added and thorough shaking is continued. The MnO_2 - asbestos is collected on a filter cone with slight suction, washed with hot water and dried at 100°C. A U-tube (diam. ¾ in., height 5½ in.), charged with this reagent and placed in front of the usual H_2CrO_4 bubbler, will absorb the bulk of the S oxides from ≃ 1100 g of steel containing up to 0·5 per cent. of S.

A. O. JONES

353. **Determination of very small carbon contents in steels.** L. Wetternik (*Mikrochim. Acta*, 1954, [5], 509–521).—Various methods are considered for determining small quantities of C in steels; it is concluded that the coulometric and conductimetric methods are the most suitable and the most accurate. These methods are described in detail. An accuracy of ± 0·002 per cent. can be attained.

A. J. MEE

354. **The sampling of nodular irons for carbon determination.** B.C.I.R.A. Methods of Analysis Sub-Committee and W. E. Clarke (*J. Res. & Dev., B.C.I.R.A.*, 1954, **5** [8], 465–468).—Four sampling techniques are investigated, three requiring drilled samples and the fourth, small solid pieces. It is concluded that the fourth technique is the only reliable one. The use of drillings is not advised because the presence in nodular irons of small amounts of fines high in carbon render it impossible to obtain a representative sample for the carbon determination.

C. J. KEATTCH

355. **X-ray analysis of foundry dusts for quartz and iron in relation to silicosis and siderosis. II. Fluorescent spectral analysis for iron.** G. L. Clark and H. C. Terford (*Anal. Chem.*, 1954, **26** [9], 1416–1418).—Standard dust samples are prepared containing known amounts of Fe mixed with SiO_2 and CaF_2, to which 20 per cent. of CaF_2 is added as an internal standard. The fluorescent spectrometer is calibrated by plotting the ratios of the corrected intensities of the FeK_α and the NiK_α lines against the percentage of Fe, when a linear graph is obtained. When foundry-dust samples are examined, 20 per cent. of Ni is added to each. The results obtained from the calibration curve are higher than those obtained by chemical analysis.

J. H. WATON

356. **Colorimetric determination of cobalt with sodium diethyldithiocarbamate.** R. Přibil, J. Jeník and M. Kobrová (*Coll. Czech. Chem. Comm.*, 1954, **19** [3], 470–476).—The intense-green colour of ethyl acetate solutions of the inner complex salt of Co^{II} with diethyldithiocarbamate is used in a sensitive method for the colorimetric determination of Co. Conditions of specificity are established. The method is applied to Co determinations in steels and minerals. [This is a translation into English of a paper that was published originally in *Chem. Listy*, 1952, **46**, 603.]

D. R. GLASSON

357. **A new photometric estimation of nickel with ethylenediaminetetra-acetic acid.** W. Nielsch and G. Böltz (*Anal. Chim. Acta*, 1954, **11** [4], 367–375).—The Ni content of solutions is determined by adding an excess of ethylenediaminetetra-acetic acid and measuring the transmittance with a Zeiss Elko II photometer and an S57E filter. The extinction is constant in the pH range 4·55 to 6·8 and in practice the soln. is buffered at ≃ 5·3 with Na acetate. High concn. of ammonium salts must be avoided. The Ni may be present originally as sulphate, nitrate, chloride or bromide without influence on the observed transmittance. Conformity to the Beer - Lambert law is obtained with Ni concn. 40 to 5000 mg per 100 ml. The method is particularly suitable for the analysis of alloys containing much Ni.

W. C. JOHNSON

358. **The determination of nickel in nickel-plating solutions.** K. E. Langford (*Metal Finish.*, 1954, **52** [9], 71–73).—After a review of the most widely used methods of nickel determination, the development of the disodium ethylenediaminetetra-acetate method is given. Applications to bright nickel solutions, reagents and the effect of magnesium are also discussed. Recommended methods in the absence of Co and Mg, in the presence of Co and the absence of Mg and in the presence of Mg and the absence of Co, are given in detail.

D. J. C. YATES

359. **Photometric determination of palladium with thiourea.** W. Nielsch (*Mikrochim. Acta*, 1954, [5], 532–538).—Palladium chloride gives a yellow complex with thiourea. The extinction coeff. of this solution is insensitive to slight variations of thiourea content in the range 360 to 380 mμ in the presence of 10 per cent. HCl soln. and at least 5 g of thiourea per 50 ml of solution. The intensity of colour remains constant for several hours after dilution to the required vol. After 15 hr. only slight variations are noted. The process is suitable for the photometric determination of Pd in the range 0·8 to 24 μg per ml of solution.

A. J. MEE

360. **Fire assay for palladium.** J. G. Fraser and F. E. Beamish (*Anal. Chem.*, 1954, **26** [9], 1474–1477).—Nine fluxes based on PbO and $Na_2B_4O_7$ with additions of SiO_2, CaO, Na_2CO_3 or KNO_3, depending on their intended use, were salted (procedure is described) with standard soln. of Pd. The salted fluxes were run down in the presence of flour according to a standard procedure (max. temp. 1200°C) and the slags were cleaned. The lead buttons were dissolved in HNO_3 and the Pd was

determined colorimetrically or gravimetrically (*Anal. Abstr.*, 1954, **1**, 1851). Records of recovery of Pd with each charge are tabulated; in general, the recovery is nearly quantitative except with acid fluxes. The behaviour of Pd - Ag alloys during cupellation is examined similarly, and losses are found to be insignificant. D. A. PANTONY

361. **Estimation of metals as sulphides. II. Estimation of platinum metals.** I. K. Taimni and G. B. S. Salaria (*Anal. Chim. Acta*, 1954, **11** [4], 329–338).—Procedures are described for the pptn. of the sulphides of Pt, Ir, Rh, Ru and Pd in a form that is readily filtered and suitable for direct weighing. The soln. containing the metal is first neutralised or made slightly alkaline with aq. NaOH or NH_3 soln. A thio salt is formed by adding a large excess of sodium or ammonium sulphide soln. (*cf. Anal. Abstr.*, 1954, **1**, 2391), the latter being a permissible alternative in the estimation of Ir and Pd; the sulphide is then pptd. by adding a large excess of acetic acid and 5 to 10 g of ammonium acetate and boiling the soln. The pptd. sulphide is filtered from the cooled soln. in a sintered-glass crucible (porosity 4), washed with water (or water containing 5 per cent. of ethanol for Rh or Ir), ethanol and ether, and dried in a vacuum desiccator. The following substances are obtained: $PtS_2.5H_2O$ (or $PtS_2.2H_2O$ if heated at 130° to 135° C); $Ir_2S_3.10H_2O$; $Rh_2S_3.3H_2O$; $Ru_2S_3.2H_2O$; $PdS.2H_2O$. Osmium yields unsatisfactory results.

W. C. JOHNSON

See also Abstracts 259, 260, 261, 263, 269, 281, 284, 415.

3.—ORGANIC ANALYSIS

362. **The determination of chlorine in pentachlorophenol and pentachlorophenyl laurate.** E. H. Searle and E. Bell (*J. Appl. Chem.*, 1954, **4** [8], 430–433).—The use of KOH in tetrahydrofurfuryl alcohol as a hydrolysis medium for certain industrially important chlorinated aromatic organic compounds, such as chlorinated phenols, is investigated. Such compounds are found to be hydrolysed quant. in 1 to 2 hr. with 15 to 25 per cent. KOH solutions. To determine the chlorine present (Volhard's method), it is necessary to distil off the tetrahydrofurfuryl alcohol from the hydrolysed product before dilution with water. During distillation the polyphenols formed by hydrolysis are converted into a separable tarry mass, which does not interfere with the pptn. of silver chloride on the addition of silver nitrate. A procedure is outlined for the determination of the proportion of active agent present in textiles treated with polychlorinated phenols as a preservative. R. J. MAGEE

363. **Determination of carboxyl end-groups in a polyester, [viz.,] polyethylene terephthalate.** H. A. Pohl (*Anal. Chem.*, 1954, **26** [10], 1614–1616).—A semimicro procedure for the determination of carboxyl end-groups in polyethylene terephthalate is described. The polymer (0·1 to 0·2 g) is dissolved in benzyl alcohol (5 ml) at 203° C, cooled and then rapidly poured into $CHCl_3$ (10 ml). The tube is rinsed with 5 ml of benzyl alcohol, and the soln. is titrated to phenol red indicator with 0·1 *N* NaOH. A coefficient of variation of 1·78 per cent. was obtained from ten determinations. G. P. COOK

364. **Determination of alkoxyl groups. V. Improved methods for the selective determination of methoxyl groups and for the simultaneous determination of methoxyl and ethoxyl groups.** G. Gran (*Svensk Papperstidning*, 1954, **57**, 702–708).—Willstätter and Utzinger's trimethylamine method for the selective determination of methoxyl group was improved by use of *iso*propanol instead of ethanol as solvent for the trimethylamine. Tetramethylammonium iodide is so little soluble in a 10 per cent. solution of trimethylamine in *iso*propanol that no solubility correction is necessary. The ppt. forms quickly and can be filtered off immediately after distilling the sample with HI. The remaining alkoxyl groups can be determined in the filtrate. The absorption and filtration arrangements have been improved. The precision of the determinations is ± 2 per cent. with samples containing about 5 mg of methoxyl and ethoxyl groups.

S. V. SERGEANT

365. **Temperature dependence of absorbance in ultra-violet spectra of organic molecules.** V. A. Yarborough, J. F. Haskin and W. J. Lambdin (*Anal. Chem.*, 1954, **26** [10], 1576–1578).—The variations of absorbance with temp. of the sample in the u.v. spectra of 19 organic compounds have been studied over the range 5° to 33° C. Methanol and *iso*octane were used as solvents. The variation ranges from 0 per cent. per °C for acetone and hexane-2:5-dione to 0·74 per cent. per °C for toluene. In general the absorbance decreases linearly with increasing sample temp.

G. P. COOK

366. **Polarography of organic compounds.** F. Freese (*Chem. Weekbl.*, 1954, **50** [45], 781–785).—A review of the various factors affecting the polarography of organic compounds is given. The relation between the polarogram and the structure of the mol. and the effect of the solvent on the polarogram are considered. The effect of the pH of the solvent generally makes it necessary to work with buffered solutions. The effect of adsorption on the polarograms of organic compounds is also discussed. Applications of polarography to the determination of the speed of reaction and the determination of the constitution of organic compounds are mentioned. A. J. MEE

367. **Rapid method for the determination of unsaturated gaseous hydrocarbons by anodic halogenisation.** K. Bratzler and H. Kleemann (*Erdöl u. Kohle*, 1954, **7** [9], 559–561).—Olefins are readily halogenated and brominated if the Br added to the gas mixture is produced electrolytically and not added in the elementary state, the gas mixture being passed round the anode where the Br is liberated. The apparatus is described. The process is useful for the determination of the olefin content of the residual gases in the Fischer - Tropsch synthesis and of coke-oven gas, *i.e.*, for gases with a low olefin content. The method can be adapted for the determination of mixtures of olefins; by use of a photo-electric cell it can be made automatic. A. J. MEE

368. **Rapid identification of glycols in alkyd resins.** C. B. Jordan (*Anal. Chem.*, 1954, **26** [10], 1657–1658).—A qualitative method for detecting vicinal glycols of low mol. wt in alkyd resins is described. These glycols are separated from other polyhydric alcohols by a reflux distillation procedure and xylene as the refluxing medium. By making use of a ternary azeotropic mixture formed by xylene, the glycols and water, the glycols are detected in aq. soln. by the standard periodate

procedure. Satisfactory results were obtained with samples containing > 5 per cent. of glycols of low mol. wt. G. P. Cook

369. **Quantitative determination of sugars on paper chromatograms by a reflectance method.** R. M. McCready and E. A. McComb (*Anal. Chem.*, 1954, **26** [10], 1645–1647).—Direct reflection density measurements on paper chromatograms of the coloured spots developed from reducing sugars and aniline - trichloroacetic acid or from fructose and derivatives with acid - resorcinol are used in the proposed method for determining sugars. The logarithm of the sugar concn. and the reflection density of light at 515 mμ follow a linear relationship over the range 25 to 125 μg of sugar per spot. Calibration curves for glucose, galactose, arabinose, and galacturonic and digalacturonic acids are illustrated. The type of paper used is not critical and the greatest consistency is attained when 2 to 5 μl of sugar soln. are applied to the paper. The method is particularly useful in the determination of pentose mixtures containing uronic acid, as orcinol methods do not distinguish between these substances. G. P. Cook

370. **Paper-chromatographic separation of sucrose, glucose, fructose and sorbitol.** R. Huygens and J. Casimir (*Bull. Inst. Agron. Stations Rech. Gembloux*, 1953, **21** [3–4], 8–13).—The problem of separating polyalcohols, *e.g.*, sorbitol, from an admixture with sugars has been solved by two-dimensional paper chromatography with double development, *i.e.*, alternately twice in each direction. Good results were also obtained with prolonged single developments (150 hr.), a pad of absorbent wadding being attached to the base of the paper. The best solvent mixtures tested were pentanol - pyridine - water (1:1:2) in one direction and benzene - butanol - pyridine - water (1:5:3:3) in the other. Spraying reagents were Na taurocholate (0·5 per cent. in 10 per cent. H_3PO_4) or benzidine for the sugars and $AgNO_3$ for the sorbitol.

Sugar Ind. Abstr.

371. **Infra-red spectra of carbohydrates. V. Use of potassium bromide films.** S. A. Barker, E. J. Bourne, W. B. Neely and D. H. Whiffen (*Chem. & Ind.*, 1954, [46], 1418–1419).—The ageing of films of KBr mixed with carbohydrates prepared in the course of investigations of the infra-red spectra of the carbohydrates has been investigated. The film was made by compressing the mixture *in vacuo*. For seven compounds (methyl α-D-glucopyranoside, 2:3:6-tri-O-methyl-α-D-glucose, 2:3:4:6-tetra-O-methyl-α-D-glucose, cellobiose, maltose, laminaribiose and α-D-galactose) there were no appreciable spectral changes as the films were aged, the spectra being identical with those obtained by use of mulls in liquid paraffin. With films of α-D-glucose, β-D-glucose, β-D-mannose and α-L-xylose, there were significant changes in the spectra after a few days, strong absorption bands being reduced and new ones appearing, but a film of α-D-glucose in KCl showed no changes. Pressure appears to be necessary for the changes to occur. These changes seem to be influenced by substituents round the pyranose ring and by the stereochemistry of individual carbon atoms. A. J. Mee

372. **Contribution to the polarography of formaldehyde.** L. Šerák (*Chem. Listy*, 1954, **48** [2], 272–274).—The introduction of gaseous formaldehyde into 0·1 *N* LiOH at 0°C produces a new diffusion-controlled wave, ≃ 250 mV more negative than the kinetic wave hitherto known. In the presence of D_2O and ethanol, this wave is stable up to 20° and 15° C, respectively, and is presumably caused by the formation of soluble lower polymers of the type $H(CH_2O)_nOH$, irreversibly converted to the usual methylene glycol, $CH_2(OH)_2$ on warming.

G. Glaser

373. **Some observations on the dimedone method for the gravimetric determination of formaldehyde.** D. Spencer and T. Henshall (*Anal. Chim. Acta*, 1954, **11** [5], 428–430).—The variation with pH and with temp. of the second-order rate constant of the reaction of dimedone with formaldehyde has been determined. The rate increases to a max. at pH 8·5 and is ≃ 6 times greater at 45°C than at 25°C. The following gravimetric method is evolved from these results. *Procedure*—Dissolve 0·80 g of dimedone in 15 ml of ethanol and dilute to 1 litre with phosphate - citric acid buffer soln. of pH 8·0. To an aq. soln. containing ≯ 15 mg in 50 ml, add 200 ml of the dimedone soln. and set aside for 12 hr. at room temp., or 2 hr. at 50° C. Acidify at room temp. with 25 ml of conc. HCl, filter through a G3 sintered-glass crucible, wash the ppt. with water, dry at 105° to 110°C and weigh.

W. C. Johnson

374. **Polarographic determination of chloroacetaldehydes. Analysis of mixtures.** P. J. Elving and C. E. Bennett (*Anal. Chem.*, 1954, **26** [10], 1572–1575).—Methods for the polarographic determination of (*a*) chloroacetaldehyde alone, (*b*) chloral hydrate in the presence of dichloro- and chloroacetaldehyde and (*c*) dichloro- or chloroacetaldehyde in presence of chloral hydrate are given. For (*a*), a 1 to 4 m*M* soln. of dichloro- or chloroacetaldehyde or a 0·4 to 2·0 m*M* soln. of chloral hydrate is made up in NH_3 buffer soln. of ionic strength 1·0 and pH 8·4 and is polarographed between −0·5 and −1·9 V *vs.* the S.C.E. Borate buffer at pH 9·2 can be used for the determination of chloral hydrate and chloroacetaldehyde. For (*b*), the aliquot containing ≃ 0·5 to 2·0 m*M* of all constituents is diluted with borate buffer and polarographed. For (*c*), the sample is diluted so that the chloral hydrate concn. is < 0·40 m*M* and the concn. of the other aldehyde is 1 to 3 m*M*; either ammonia or borate buffer is used. Mixtures of dichloro- and chloroacetaldehyde cannot be determined directly as the two compounds give coincident waves. The precision of the methods is ≃ ± 3 per cent. G. P. Cook

375. **Analytical applications of the cyanohydrin reaction.** W. J. Svirbely and J. F. Roth (*Anal. Chem.*, 1954, **26** [8], 1377–1378).—NaCN reacts completely with acetaldehyde and propionaldehyde within the pH range 5·2 to 6·8 (bromocresol purple). Experiments suggest that this reaction could be used as the basis for quant. determination of the aldehydes and the quant. determination of halide ions in the presence of cyanide. G. P. Cook

376. **A system of characterisation of common organic acids.** R. T. Wendland and D. H. Wheeler (*Anal. Chem.*, 1954, **26** [9], 1469–1474).—The classification is based on the following considerations. Class I acids include liquid acids melting at 30° C or lower; it is subdivided according to odour, miscibility with water, density, character of alkaline soln., reaction with aq. $KMnO_4$ and determination of neutral equivalent. Classes II and III represent solid saturated and unsaturated acids, respectively; these are subdivided according

to m.p., neutral equivalent, reaction with $KMnO_4$ and Br and, for low-melting solids, water miscibility and nature of alkaline soln. Class IV acids are solid phenolic acids and are distinguished from the others by giving deep colorations with aq. $FeCl_3$ and having high m.p. Classification of the drying-oil acids requires the determination of the iodine number, the examination of the u.v. absorption spectrum, the preparation of bromo and hydroxy derivatives, the alkali isomerisation of non-conjugated acids to conjugated forms and quant. determination by u.v. absorption. G. P. Cook

377. **Spray reagent for the identification of certain organic acids in paper chromatography.** P. Godin (*Chem. & Ind.*, 1954, [46], 1424).—Fürth and Herrmanns' reagent (7 vol. of pyridine with 3 vol. of acetic anhydride, mixed immediately before use) is recommended, in preference to an indicator such as bromocresol green, for spraying chromatograms of organic acids; it shows up certain acids of biological interest. At room temp., *cis*- and *trans*-aconitic acids give a brown-yellow spot (0·005 mg), fumaric acid a brown spot (0·05 mg) and itaconic acid a pale-yellow spot (0·02 mg); limits of identification are the figures in parentheses above. Citric and *iso*citric acids give a yellowish spot, but it is too weak for their detection. A large number of common organic acids do not react. A. J. Mee

378. **Maleic and fumaric acids. Origin of split polarographic waves and analytical significance.** P. J. Elving and I. Rosenthal (*Anal. Chem.*, 1954, **26** [9], 1454–1459).—Maleic and fumaric acids have been investigated systematically over the pH range 0·7 to 12 with different buffers at various ionic strengths. At $\simeq$ pH 5·0 the original wave of each acid begins to decrease and a secondary more negative wave begins to appear. The height of the latter for maleic acid increases up to pH 8·0 and then decreases until at pH 10 it is almost non-existent; the fumaric acid secondary wave does not diminish until pH 10 is reached. Total diffusion currents of the two waves are approximately equal to that of the single wave at low pH values. The relation of this wave-splitting phenomenon to the kinetics of the acid - anion equilibrium and to the nature of the $E_{\frac{1}{2}}$ - pH relationship is discussed. Recommendations for the modification and improvement of existing methods for maleic and fumaric acid determinations are suggested. To attain good reproducibility for these waves, precise pH and temp. control is essential. G. P. Cook

379. **A specific enzymatic micro-method for the determination of acetate.** R. W. von Korff (*J. Biol. Chem.*, 1954, **210** [2], 539–544).—The proposed method was developed for the determination of acetate formed during the oxidation of pyruvate by heart-muscle mitochondria. It involves spectrophotometric determination of the amount of reduced diphosphopyridine nucleotide formed in a coupled reaction of acetate-activating enzyme, malic dehydrogenase and condensing enzyme. An enzyme preparation from rabbit-heart ventricle contains sufficient of these three enzymes. The method is used for determination of μg amounts of acetic acid; formate, propionate, butyrate, acetoacetate and fluoroacetate do not interfere. Pyruvate and Na^+, if present, must be removed by simple vacuum-distillation of the volatile acids. Before determination, the acid samples are neutralised to pH 6·5 with KOH. For a determination, the following reaction mixture is prepared: 0·2 *M* glutathione (0·05 ml), a 1 mg per ml soln. of coenzyme A (70 to 80 per cent. purity) (0·1 ml), *M* aminotri(hydroxymethyl)methane at pH 9·5 (0·05 ml), 0·2 *M* malate (0·05 ml), 1 per cent. diphosphopyridine nucleotide (0·05 ml), 0·04 *M* dipotassium adenosinetriphosphate (0·05 ml), 0·06 *M* $MgCl_2$ (0·10 ml) and the sample, and water to give a total 1·46 ml. The enzyme prep. (0·04 ml) is added, and the mixture is incubated at 37°C for 30 min. The samples are then diluted with 0·5 *M* phosphate buffer at pH 7·5 (2·0 ml), and the optical density at 340 mμ is determined spectrophotometrically against a control containing no acetate. Standard acetate samples are used as internal standards. J. N. Ashley

380. **Cerate oxidimetry. I. Oxidation of formic, glycollic, malic, malonic and tartaric acids.** N. N. Sharma and R. C. Mehrotra (*Anal. Chim. Acta*, 1954, **11** [5], 417–427).—Willard and Young (*Brit. Abstr. A*, 1930, 312) observed only slight oxidation of formic acid with Ce^{IV} salts and obtained only empirical factors for the reaction of Ce^{IV} with tartaric and other acids. It is now shown that formic acid is quant. oxidised when heated in a bath of boiling water for 50 min. under a reflux condenser with an excess of 0·1 *N* $Ce(SO_4)_2$ previously mixed with conc. H_2SO_4 (2 vol. to 1 vol. of the other reactants); the excess of Ce^{IV} is titrated, after dilution, with standard $Fe(NH_4)_2(SO_4)_2$. Tartaric acid is quant. oxidised to carbon dioxide and water by heating in a bath of boiling water with an excess of 0·1 *N* $Ce(SO_4)_2$ for 10 to 15 min., adding 2 vol. of conc. H_2SO_4 and heating for a further 50 min. If the H_2SO_4 is added at the beginning of the reaction, the oxidation requires a much longer time. Malonic, malic and glycollic acids are also oxidised quant. under the same conditions as tartaric acid. W. C. Johnson

381. **The polarographic determination of microgram quantities of oxalic acid [by means of a europium solution].** G. F. Reynolds and R. C. Smart (*Anal. Chim. Acta*, 1954, **11** [5], 487–494).—Oxalate (50 to 125 μg) is determined by mixing it with an excess of a standard soln. of europium (14·5 mg of europium oxide in 2·0 ml of 10 *M* HCl, diluted to 10 ml) and determining, polarographically, the unprecipitated excess of Eu. The polarogram is taken at −0·4 to −1·1 V *vs.* the mercury pool, and the step occurs at − 0·8 V. The step height is unaffected by concn. of oxalic acid < 6 μg per ml. Ammonium salts do not interfere, but Fe and Cr salts must be absent. The polarography of Eu is discussed. W. C. Johnson

382. **The quantitative determination of ethylenediamine.** F. v. Gizycki (*Z. anal. Chem.*, 1954, **143** [5], 350–352).—Ethylenediamine is determined by measuring the vol. of N evolved in the quant. reaction with HNO_2. D. R. Glasson

383. **Using mass spectrometry in aromatic hydrocarbon analyses.** J. H. Shively and J. J. Morello (*Petrol. Process.*, 1954, **9** [4], 554–555).—Methods available for determining aromatic hydrocarbons in petroleum naphthas are discussed; the use of mass spectrometry is stressed. A typical analysis is given for such components as benzene, toluene, ethylbenzene and xylene. Advantages of mass spectrometry over other methods of analysis are reviewed. J. Inst. Petrol

384. **Determination of guaiacol in presence of large amounts of catechol.** D. H. Rosenblatt, M. M. Demek and J. Epstein (*Anal. Chem.*, 1954, **26** [10],

1655–1656).—Guaiacol with 4-aminophenazone (**I**) forms a dye that can be extracted with $CHCl_3$; the absorbance of the dye at 460 mμ gives a measure of the guaiacol content of the sample. The pH is adjusted to between 10·45 and 10·55, before $K_3Fe(CN)_6$ reagent and **I** is added. Beer's law is obeyed between 0 and 0·6 p.p.m. of guaiacol in a constant catechol concn. $< 2{\cdot}5 \times 10^{-4}$ *M*.

G. P. Cook

385. **Polarographic procedure for the analysis of a technical product. Estimation of maleic anhydride and 1:4-naphthaquinone in phthalic anhydride.** E. Barendrecht (*Chem. Weekbl.*, 1954, **50** [45], 785–791).—Phthalic anhydride is manufactured by the catalytic oxidation of naphthalene; 1:4-naphthaquinone is an intermediate product and a little maleic anhydride may be formed. The determination of these compounds in phthalic anhydride is therefore important, and a polarographic method for determining them has been developed. The polarographic curves of maleic and fumaric acids and of 1:4-naphthaquinone are given. For the estimation of 1:4-naphthaquinone, a weighed amount of the substance is dissolved in 100 ml of acetone; to 5 ml of the soln. are added 40 ml of Britton - Robinson buffer and the whole is made up to 100 ml with water. The solution is polarographed; $E_{\frac{1}{2}} = +0{\cdot}12$ V *vs.* the S.C.E. For the estimation of maleic acid, the weighed sample is dissolved in the least quantity of acetone required to dissolve it. Fifty ml of 0·2 *N* HCl soln. are added and the mixture is heated on a steam-bath. The phthalic anhydride and 1:4-naphthaquinone are precipitated. The liquid is filtered and made up to 100 ml. The solution is extracted twice with 25 ml of benzene, and the aq. substrate is polarographed; $E_{\frac{1}{2}}$, $-0{\cdot}68$ V *vs.* the S.C.E. Neither the 1:4-naphthaquinone nor the maleic acid concn. should be greater than 2×10^{-3} *M*.

A. J. Mee

386. **Chromatography of aromatic amines on paper.** J. Bertetti (*Ann. Chim., Roma*, 1954, **44** [7–8], 495–499).—R_F values are reported for 45 aromatic amines chromatographed on paper in butanol saturated with 25 per cent. aqueous acetic acid; a solution of potassium dichromate in sulphuric acid is used as developer; this enables a number of amines with R_F values near to one another to be identified by differences in the colour of the stains. The developing action of furfural, ferric chloride, bromophenol blue and ninhydrin is also investigated.

R. C. Murray

387. **Polarographic determination of sulphones.** E. S. Levin and A. P. Shestov (*Dokl. Akad. Nauk, SSSR*, 1954, **96** [5], 999–1003).—A study of the polarograms of diphenyl sulphone, benzene-1:3-disulphonyl chloride and (diphenyl sulphone)-3:3′-disulphonyl chloride indicates that polarography is a general method for analysis of sulphones as sulphonic acid groups cause no interference. It is thought that the electrode reaction is: $R_2SO_2 + 2H_2O + 2e \rightarrow R{\cdot}SO_2H + RH + 2\,OH'$.

R. C. Murray

388. **Determination of pyridinium nitrogen.** F. E. Crane, jun., and R. M. Fuoss (*Anal. Chem.*, 1954, **26** [10], 1651–1652).—Pyridinium salts are converted to aliphatic cleavage products by the action of alkaline peroxide (Na_2O_2 + water); the N can then be quantitatively determined by standard procedures. In order to obtain max. recovery, a twenty-fold excess of Na_2O_2 is essential. Approximately 75 per cent. of the N is carried over as the amine or as NH_3 during the first distillation procedure, the remaining N being determined by the Kjeldahl method. With methylpicolinium iodide as a test compound, 5·84 ± 0·13 per cent. of N was found from 14 analyses; the theoretical amount was 5·96 per cent.

G. P. Cook

389. **On the fluorimetric determination of N-methylnicotinamide.** H. L. Rosenthal (*Science*, 1954, **120**, 231).—Pretreatment of samples with alkaline or neutral H_2O_2 (*Science*, 1952, **116**, 462) may completely destroy N-methylnicotinamide, depending on the concn. and reaction time, but is effective in intensifying fluorescence if H_2O_2 is added after acetone and alkali. Rigid control of H_2O_2 concn. is necessary for reproducible results. A large number of inorganic elements catalyse formation of a fluorescent derivative. Ir and Ce salts have the greatest activity at concn. of 5×10^{-6} and 8×10^{-6} *M*, respectively, being almost 1000 times more active than H_2O_2 at optimum concn.

H. F. W. Kirkpatrick

390. **Alumina-adsorption analysis of petroleum aromatics in 420° to 600°-F range.** C. M. McKinney and R. L. Hopkins (*Anal. Chem.*, 1954, **26** [9], 1460–1465).—A method for the determination of aromatics in the 420° to 600° F fraction of distillate fuels is described. The aromatic fraction is obtained by a silica-gel absorption procedure and the concentrate is introduced into a column of alumina. Monocyclic aromatics are eluted with *n*-pentane and desorption with *iso*propanol gives polycyclic aromatics and, probably, sulphur-containing compounds. The fractions are studied by density and refractive-index measurements. The accuracy of the method when applied to distillates is not known, because the composition of petroleum over the distillation range is not known; sulphur-containing compounds appear to be the greatest cause of error. Results from synthetic blends of mono- and di-cyclic aromatics were accurate to within 1 per cent. of known values. Accuracy of the polycyclic aromatic determination for distillates low in S content is believed to be $\simeq \pm 3$ per cent.

G. P. Cook

391. **The identification of di- and polyamines and aminohydroxy compounds as fission products of azo dyestuffs.** E. D. G. Frahm (*Rec. Trav. Chim. Pays-Bas*, 1954, **73** [9–10], 748–758).—Dilute solutions of compounds such as *p*-phenylenediamine, 1:2:4-triaminobenzene, 2-amino-4-chlorophenol or 5-aminosalicylic acid, resulting from reduction of azo dyes, can be benzoylated (either directly or after separation of one or more of the fission products) and the m.p. of the resulting benzoyl deriv. can be determined, the yield of any deriv. being approximately quantitative. Any volatile amine or sparingly soluble diamine should be removed before benzoylation. Benzoyl deriv. insoluble in alkaline media can be recrystallised (as the Na salt) from hot water, or by fractional crystallisation of a mixture of similar deriv. ON-benzoyl deriv. of aminohydroxy compounds can be saponified to the N-benzoyl deriv. Those deriv. soluble in alkaline media are pptd. on acidification with HCl, the benzoic acid being removed with hot water. All benzoyl deriv. can be obtained pure by crystallisation from hot acetic acid. When the reduction products contain a diaminodiarylurea or acylated diamine, *e.g.*, *m*-aminobenzoyl-*m*-phenylenediamine, refluxing with 10 to 20 per cent. H_2SO_4 will convert these compounds into diamines. The method has been successfully applied to a large number of

azo dyes, including the Chlorantine fast and Coprantine groups. The detailed procedure for Chrome fast orange R and Solar orange 2 RN is described, and the m.p. of some benzoyl deriv. not listed in the literature are given. W. J. BAKER

392. **A chromatographic separation of the aminofluorescein isomers.** J. de Repentigny and A. T. James (*Nature*, 1954, **174**, 927–928).—The two isomeric aminofluoresceins obtained by condensation of resorcinol with 4-nitrophthalic anhydride and subsequent reduction are completely separated by chromatography on kieselguhr. The stationary phase is sodium phosphate buffer, pH 8·0, and the mobile phase is *n*-butanol containing 35 per cent. v/v of *cyclo*hexane. The process can be hastened by gradient elution, the initial concn. of *n*-butanol then being 35 per cent. v/v. The method is only suitable for a small-scale separation, but gives much larger yields than does fractional crystallisation of the isomers. C. E. SEARLE

393. **Near infra-red absorption spectra of natural and synthetic fibres.** A. Elliott, W. E. Hanby and B. R. Malcolm (*Brit. J. Appl. Phys.*, 1954, **5** [11], 377–381).—The near infra-red absorption spectra with polarised radiation of natural and synthetic fibres have been examined. In this region, bands are either overtones or combinations of the fundamental vibrations with low absorption coeff., so a specimen approx. 0·2 mm in diameter can be used. A suitable source is a tungsten-filament lamp in glass and the spectrometer prism may be of second-quality fused quartz; a lead sulphide cell can be used as detector with an 800-c.p.s. amplifier. The uncertain origin of bands in the region is a disadvantage. The spectra of poly-L-alanine, polyglycine, wool, silks and commercial regenerated protein fibres are shown and discussed. Information can be obtained on the orientation and mol. configuration of fibres. Examination of the spectra of regenerated protein fibres shows that there is still a small amount of extended protein present. A nearly constant proportion of folded configuration is present in the silk fibres and steam-stretched poly-L-alanine examined. A. J. MEE

394. **Rapid identification of wet-strength resins in paper.** J. C. Barthel (*Paper Tr. J.*, 1954, **138** [37], 24).—*Reagents*—Dissolve 1 g of phenylhydrazine in 41·7 g of 96 per cent. H_2SO_4 diluted with 8·3 g of H_2O, and dilute the solution to 100 g (soln. A). Dissolve 10 g of $FeCl_3$ in water to make up 100 g (soln. B).

Procedure—Allow a drop of soln. A to spread over a small area (*ca.* 2·3 cm diam.) of the paper with the aid of a glass rod, and blot off the excess of liquid after 30 sec. Add a drop of soln. B, when in the presence of melamine - formaldehyde or urea - formaldehyde resin a pink to red or reddish brown colour develops. Solution A hydrolyses the resin forming formaldehyde phenylhydrazone, which is converted by soln. B to an intensely coloured Fe complex. S. V. SERGEANT

395. **Colorimetry as applied to oils.** H.-D. Schulz-Methke (*Erdöl u. Kohle*, 1954, **7** [8], 501–503).—The general principles of colorimetric determinations as applied to oils are described. Mention is made of the technique of visual comparison of colour, whilst colorimetric determinations with instruments are described and illustrated by means of two types of colorimeters incorporating photocells in their optical systems. Colorimetric measurements can also be used to investigate compositions of oils and to explain reaction mechanisms. C. J. KEATTCH

396. **Determination of the ageing of oils.** O. Widmaier (*Erdöl u. Kohle*, 1954, **7** [9], 569–572).—Oxygen was passed through oils at 190°C at the rate of 5 ml per sec. for 3 hr.; the acids, aldehydes and ketones formed were determined by the usual methods. There are two main oxidation stages. In the primary stage, aldehydes, ketones, acids, CO and CO_2 are formed. In the secondary oxidation, high polymers such as resins and asphalt, which are insol. in benzene, are formed. A. J. MEE

397. **Principles of elution chromatography as applied to separation of lubricating-oil components.** G. E. Irish and A. C. Karbum (*Anal. Chem.*, 1954, **26** [9], 1445–1451).—A study of the variables that influence chromatographic separation of lubricating-oil components is presented. It was found that precise and accurate separations could be made, provided that the column was not overloaded. The max. column load for separations of two classes of oil components was principally dependent upon the classes of the components, the type of eluent and the type of adsorbent. Generally, although the chromatograms do not accurately reflect the spread of the properties of the components, quant. separation into aromatic classes may be made. G. P. COOK

398. **Analysis of synthetic anionic detergent compositions.** R. House and J. L. Darragh (*Anal. Chem.*, 1954, **26** [9], 1492–1497).—Methods for the analysis of anionic detergents are described, especially those for the determination of active ingredient and colour. The methods were mainly applied to alkyl sulphate and alkylbenzenesulphonate detergents. For assay, the titration procedure of Epton (*Trans. Faraday Soc.*, 1948, **44**, 226) was modified to give greater accuracy, the improvement being made by use of a more stable quaternary ammonium halide soln. as titrant and application of a more convenient standardisation procedure. Inorganic SO_4'' is determined by modification of the method of Ogg, Willits and Cooper (*Brit. Abstr. C*, 1948, 85), and sulphonate additives of low mol. wt. are measured by extraction of the aq. detergent soln. with diethyl ether, extraction of the latter with HCl soln. and inspection in the u.v. region of the spectrum. The colour of the sample is measured by absorbance or transmittance readings with a tristimulus filter. G. P. COOK

399. **Analytical techniques for varnish resins.** A. Poluzzi (*Ind. Vern.*, 1954, **8**, 61–66, 93–97, 147–152, 175–181).—This detailed review of published methods covers synthetic as well as natural resins. (54 references.) D. R. DUNCAN

400. **Photocolorimetry in the ink industry.** J.-E. Goris (*Chim. Peint.*, 1954, **17** [3], 95–97).—Fountain-pen inks may be compared in 0·5 or 1 per cent. solution by the use of six colour filters. Colour changes produced on drying and ageing may be followed by reflection photocolorimetry. L. A. O'NEILL

401. **Determination of the artificial resin-binding agent content [in floor coverings with polyvinyl acetate basis].** E. Gollmer (*Kunststoffe*, 1954, **44** [9], 383–384).—The sample (5 to 10 g) is dried for 1 hr. at 100°C and for 6 hr. at 105°C, and extracted with ethanol for 16 hr. The residue is dried at

105° C for 1 hr., weighed and pulverised. The material so obtained is boiled with ethanol, filtered off, and hydrolysed by 0·5 *N* ethanolic KOH for 1 hr. The polyvinyl alcohol is dissolved in water and the residual filler is weighed. The percentage of artificial resin is (100 −percentage of filler).

H. WREN

402. **Vegetable tanning: IX. A study of several methods for determining the natural acidity in vegetable tanning liquors. Part I.** D. Burton and J. C. Bickley (*J. Soc. Leath. Tr. Chem.*, 1954, **38** [8], 249–260).—Methods are described for determining the following constituents in a vegetable tanning liquor: (*a*) acidity due to free carboxyl groups of pyrogallol tannins ("tannin acids"), (*b*) salts of tannin acids, (*c*) acidity due to the natural acids and (*d*) salts of the natural acids. The sum of (*a*) + (*c*) is determined by titration with 0·5 *N* NaOH soln. to pH 5·8, (*c*) by passing the liquor through a "Naturin" (synthetic skin) membrane and titrating the dialysate, and (*c*) + (*d*) by passing a portion of the dialysate through a base-exchange resin. Total salts minus (*d*) gives (*b*). In chromatography on hide-powder columns, gallic, lactic and acetic acids can be quantitatively recovered; under the same conditions, however, myrobalans, valonia and mimosa liquors yield corresponding fractions containing less tannin acids than the amounts found by the dialysis method.

E. HAYES

403. **Evaluation of chemical protectants as inhibitors of ozone-induced degradation of GR-S [synthetic rubber].** A. D. Delman, B. B. Simms and A. R. Allison (*Anal. Chem.*, 1954, **26** [10], 1589–1592).—A method is described for the evaluation of chemical protectants for inhibiting ozone deterioration of GR-S and other elastomeric materials; it is based on the rate of change in viscosity of polymeric solutions of these material when treated with ozone. GR-S was purified by extraction with a mixture of ethanol - toluene azeotrope and 10 per cent. H_2O, and the purified polymer was dried to constant wt. This material was dissolved in *o*-dichlorobenzene and aliquots were treated with ozonised O and the various chemical protectants under investigation. Viscosity measurements were made on these solutions at different time intervals. Representative curves for several chemical additives recommended for elastomer formulations are given.

G. P. COOK

404. **Polarographic determination of 2:4:6-trinitrotoluene and *cyclo*trimethylenetrinitramine in explosive mixtures.** D. T. Lewis (*Analyst*, 1954, **79**, 644–648).—A polarographic method is described for micro-determination of 2:4:6-trinitrotoluene and *cyclo*trimethylenetrinitramine. Samples weighing $\simeq$ 1 mg can be assayed with an error of $\pm$ 2 per cent., but with macro amounts classical methods of gravimetric analysis would be more accurate. The half-wave potentials are observed in acetone soln. and de-oxygenation is effected by use of a base soln. of 0·05 *M* Na_2SO_3 and $Na_2B_4O_7$, thus avoiding both the wave due to dissolved O and the loss of solvent caused by a stream of N. Trinitrotoluene shows reduction waves at −0·51, −0·65 and −1·05 V, and, as the method is based on observation of the first and most stable wave, use of a suppressor is unnecessary. *cyclo*Trimethylenetrinitramine gives a single well-defined wave at −0·77 V against the S.C.E. at 25°C. The Ilkovič equation is shown to apply for the quant. determination of the nitro compounds in the medium used.

A. O. JONES

405. **Adsorption chromatography and liquid partition of high polymers. Silicones.** D. W. Bannister, C. S. G. Phillips and R. J. P. Williams (*Anal. Chem.*, 1954, **26** [9], 1451–1454).—Two countercurrent methods were examined as fractionating techniques to determine the mol. wt. distribution in high polymers. The experiments were carried out on silicone polymers known to be linear. The first method consisted in gradient elution, with carbon as the adsorbent and ether in methanol as the eluting solvent. The mol. wt. of the fraction was found to increase with the eluting volume. The second method of liquid - liquid partition in a vortex column was applied with success to the fractionation of low mol. wt. substances. Both methods were rapid and the fractionations were sharp.

G. P. COOK

See also Abstracts 293, 325, 332, 379, 516, 517, 526.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

406. **Polarography in biochemistry.** J. de Wael (*Chem. Weekbl.*, 1954, **50** [45], 778–780).—The application of polarography to the detection and determination of metals of biological importance (Cu, Pb, Tl, Zn) is discussed; results are given for the determination of these metals in the organs of animals poisoned by them. The polarography of proteins in the presence of Co salts is also considered. The application of polarography to the investigation of ketosteroids and their determination in biological fluids is described.

A. J. MEE

407. **The accuracy of direct determination of oxygen and carbon dioxide tensions in human blood *in vitro*.** G. F. Filley, E. Gay and G. W. Wright (*J. Clin. Invest.*, 1954, **33** [4], 510–516).—Two modifications to the Riley bubble method (*J. Biol. Chem.*, 1945, **161**, 621) are described which increase the precision by reducing dependence upon technical skill. The first is a microscope reading-device for measuring the bubble length to the nearest 0·1 mm; the second is a procedure for absorption that prevents entry of alkaline reagents into the mid-position of the capillary, where the bubble length is measured.

H. F. W. KIRKPATRICK

408. **Testing urine for acetone.** W. Swallow (*Chem. & Drugg.*, 1954, **162**, 65).—Rothera's test for acetone can be made roughly quantitative by comparison with standards containing known amounts of acetone. A standard procedure that gives consistent results is described.

I. JONES

409. **Quantitative determination of serum sodium involving separation of cations on a resin column.** J. C. Vanatta and C. C. Cox (*J. Biol. Chem.*, 1954, **210** [2], 719–732).—A new method for the determination of Na in serum is described; it needs ouly 1 ml of serum and 2 hr. to complete. The method involves separation of the Na from other cations by elution from a cation-resin column (Amberlite IR-112) with 0·05 *M* $BaCl_2$, pptn. of the Ba as $BaSO_4$ and conversion of the NaCl into NaOH on an anion-resin column (Amberlite IRA-400). The NaOH is then titrated with 0·01 *N* HCl. The results agree within 1 per cent. with those obtained by the method of Butler and Tuthill (*Brit. Abstr. A*, 1931, 1342). The main errors are from a blank error caused by the anion resin and occlusion of Na

in the pptn. of $BaSO_4$. If these procedures are carefully controlled, the errors can be evaluated and corrections applied. J. N. ASHLEY

410. **A quick and simple method for blood-sugar estimation.** J. Lee (*Brit. Med. J.*, 1954, **ii**, 1087–1088).—The method of Sumner (*J. Biol. Chem.*, 1921, **47**, 5; 1924–25, **62**, 287; 1925, **65**, 393) is adapted for use in emergencies. *Procedure*—Add 0·2 ml of capillary blood to 1 ml of a 1·75 per cent. aq. soln. of 3:5-dinitrosalicylic acid, filter, and to 0·4 ml of the filtrate add 0·4 ml of alkaline reagent (13·8 g of phenol and 12·6 g of $Na_2S_2O_5$ in 350 ml of 10 per cent. NaOH added to a soln. of 510 g of Rochelle salt in 880 ml of water). Heat in boiling water for 3 min., cool and match the colour against artificial standards. The standards are available commercially and the technique is simplified by using calibrated standard-bore tubes also commercially obtainable. For less than 400 mg per 100 ml the results are usually within 30 mg of the value given by the Folin - Wu method.
H. F. W. KIRKPATRICK

411. **A method for the estimation of inulin in plasma and urine containing dextran.** J. R. K. Preedy (*J. Biol. Chem.*, 1954, **210** [2], 651–655).—A modification of the method of Roe *et al.* (*Brit. Abstr. C*, 1949, 340) for determination of inulin in plasma and urine containing dextran is described. After the removal of protein by $ZnCl_2$ - NaOH soln., the dextran is pptd. from the filtrate by the addition of ethanol; after the removal of dextran, the determination is carried out by the original method (*loc. cit.*). Plasma or urine inulin (10 to 50 mg per 100 ml) is determined satisfactorily in the presence of 100 to 1200 mg of dextran. J. N. ASHLEY

412. **Micro-determination of nicotine in rabbit urine by cyanogen bromide reaction.** I. Yamamoto, M. Takeuchi and A. Tsujimoto (*Folia Pharmacol. Japan*, 1954, **50** [1], 70–75).—König's cyanogen bromide method (*Z. angew. Chem.*, 1905, **18**, 115) was improved by adding 0·1 per cent. of aniline, adjusting the pH to 8·6 to 9·0 and measuring the absorption at 460 mμ 5 min. after adding the reagent. This method can detect nicotine above the concn. 0·5 μg per ml. Pyridine, pyrimidine, vitamin B_6 and nicotinic acid do not interfere.
CHEM. ABSTR.

413. **Researches on determination of gonadotrophins. I. Chromatographic separation of the two principal gonadotrophins in the urine of pregnant women.** P. Vignes, M. Robey and H. Simonnet (*Bull. Soc. Chim. Biol.*, 1954, **36** [8], 1163–1172).—The procedure developed for the separation of gonadotrophin A (follicle-stimulant) from gonadotrophin B (chorionic) is a refinement of the chromatographic-column method of Crooke and Butt (*Proc. Roy. Soc. Med.*, 1952, **45**, 805). The initial total absorption of the hormones on kaolin involves elution with *N* aq. NH_3 soln., centrifugation at pH 8 to remove impurities and pptn. with ethanol. The hormone extract (15 μg) is dissolved in dist. H_2O (10 ml), the insol. matter having been removed by centrifuging; to the soln. is added 10 ml of MacIntire's suspension of $Ca_3(PO_4)_2$ in sucrose (*Brit. Abstr. A I*, 1945, 173). The mixture is shaken for 20 min. and then centrifuged to separate the adsorbate from the residual liquid (*R*), which contains almost pure gonadotrophin A. By elution of the adsorbate with 10 ml of 0·002 *M* Na_2HPO_4, gonadotrophin A is obtained in the eluted soln. (*E*) mixed with a small amount of gonadotrophin B. The remainder of the latter is obtained pure by further elution of the adsorbate with ≯ 40 ml of 0·035 *M* Na_2PO_4 containing 10 per cent. w/w of NaCl. The total yield of hormones is ≃ 70 per cent.; the efficiency of separation was confirmed by tests on hypophysectomised rats and by synergy experiments. The determination of gonadotrophin A in *R* is effected by injection into young mice, and in *E* by assuming one unit as the amount that, in a mouse, trebles the action of gonadotrophin B. The latter is determined approx. from the protein content. Results for two samples of urine are reported; they confirm the theory of Lyons *et al.* (*Endocrinol.*, 1953, **53**, 674) for the gonadotrophic activity in pregnant women.
W. J. BAKER

414. **The determination of probenecid (Benemid) in body fluids.** E. K. Tillson, G. S. Schuchardt, J. K. Fishman and K. H. Beyer (*J. Pharmacol.*, 1954, **111** [4], 385)—This paper describes two methods for the determination of probenecid (*p*-di-*n*-propylsulphamylbenzoic acid) in body fluids, a spectrophotometric method and a colorimetric method. For the spectrophotometric method, add 30 ml of $CHCl_3$ to 1 ml of plasma or diluted urine and 1·0 ml of 1·0 *N* HCl and shake in a glass-stoppered bottle for 15 min. Centrifuge for 3 to 5 min. and remove the aqueous layer. Transfer 20 ml of the solvent phase to another bottle containing 5 ml of 0·1 *N* NaOH and shake for 5 min. Centrifuge for at least 5 min. and transfer about 3 ml of the aqueous phase to a quartz spectrophotometer cell and read the optical density in the Beckman spectrophotometer at 242·5 mμ. A reagent blank is run alongside and should not have an optical density greater than 0·50. As the method is not specific, blanks should be obtained from each patient before the drug is administered. The standard is prepared in concn. from 3 to 18·5 μg per ml by dilution of a stock standard with 0·1 *N* NaOH. For the colorimetric method, shake 30 ml of $CHCl_3$ with 1·0 ml of the unknown and 1·0 ml of 1 *N* HCl for 15 min. in a glass-stoppered bottle, centrifuge and remove the aqueous layer. Transfer 15 ml of the solvent phase to another bottle containing an equal volume of methylene blue reagent. Shake for 10 min., centrifuge, remove the aqueous layer and immediately read the solvent layer colorimetrically at a wavelength of 635 mμ. A reagent blank should be run alongside. The colorimetric method is preferred for clinical use as it is unaffected by most medicaments and endogenous metabolic products. G. F. SOMERS

415. **Complexones in chemical analysis. XXXVII. Polarographic determination of calcium in biological material.** R. Přibil and Z. Roubal (*Coll. Czech. Chem. Comm.*, 1954, **19** [2], 252–257).—Ca is polarographically determined in urine and blood by a method based on the displacement reaction $ZnY'' + Ca'' = CaY'' + Zn''$ (Y″ = complexonate). This reaction is quant. in 4 to 6 *N* aq. NH_3. Interference by Mg is prevented by pptg. it as $MgNH_4PO_4$. [This is a translation into English of a paper published originally in *Chem. Listy*, 1953, **47**, 189.]
D. R. GLASSON

416. **Small-scale filter-paper chromatography. Factors affecting the separation and sequence of amino-acids.** J. C. Underwood and L. B. Rockland (*Anal. Chem.*, 1954, **26** [10], 1553–1557).—The relationships between solvent character, water content of the solvent, acidic and basic solvent supplements, filter-papers and the separation and

sequences of the amino-acids on small-scale filter-paper chromatograms were studied. The sequence of the 20 amino-acids examined was independent of the 9 solvents and 3 filter-papers used, but considered as independent groups (acidic, basic, neutral and cyclic amino-acids) the sequences were influenced mainly by the acidity or basicity of the solvent. Solvents containing acids such as formic acid tended to improve separation and reproducibility, and the result was the same when water was present in the solvent for all except the acidic group. Solvents containing ammonia have similar effects. The most satisfactory separations of individual amino-acids were obtained with *tert.*-butanol - water - formic acid and phenol - water - aq. ammonia systems. G. P. Cook

417. **Improvement in the technique of identifying minimal amounts of amino-acids on paper chromatograms.** W. Kellner, H. Hellmuth and H. Martin (*Naturwissenschaften*, 1954, **41** [13], 304).—The test solution is applied as a streak to the paper and developed in the usual way. After drying, the strip is stood on edge in a Petri dish containing some distilled water. As soon as the water front has reached the upper edge of the paper the strip is dried and stained with ninhydrin. The material can be concentrated 4 to 8 times in this way and areas previously negative may show positive spots. E. Kawerau

418. **Improved bacterimetric method for cystine.** G. D. Shockman, J. J. Kolb and G. Toennies (*Anal. Chem.*, 1954, **26** [10], 1657).—The microbiological method of Riesen *et al.* (*J. Biol. Chem.*, 1947, **171**, 731), in which *Leuconostoc mesenteroides* PD–60 in their oxidised peptone medium is used, has been modified to increase sensitivity and to reduce incubation time. The precision is 2 to 3 per cent. on hydrolysed materials and the sensitivity is 0·22 μg per ml. G. P Cook

419. **Thread-electrophoresis, a method for the electrophoretic separation of very small amounts of proteins. (Preliminary communication.)** H. G. Nöller (*Klin. Wochschr.*, 1954, **32** [41–42], 988–989).—Very small amounts of protein can be separated by means of electrophoresis on artificial-silk threads mounted between two pieces of filter-paper moistened with buffer solution in contact with electrodes. A potential gradient of 10 V per cm is applied for 8 to 20 hr. The positions of the protein fractions are determined either by staining with radioactive dye-stuffs or by running proteins previously marked with radioactive I, and detection of the radioactive areas by autoradiography or by a Geiger counter. G. W. Cambridge

420. **Identification of amino-sugars by paper chromatography.** P. J. Stoffyn and R. W. Jeanloz (*Arch. Biochem. Biophys.*, 1954, **52** [2], 373–379).—A procedure is described for separating, identifying and estimating 2 to 5 μg of glucosamine or galactosamine in the presence of up to 100 μg of the other amine-sugar. By preliminary treatment with ninhydrin and pyridine, either in a capillary tube or on filter-paper, the amino-sugars are degraded to arabinose and lyxose, respectively, and are then separated chromatographically. In the presence of amino-acids and neutral sugars, a two-dimensional procedure is necessary. The strip carrying the amino sugar spots, separated in the first run, is cut out, the paper is treated with ninhydrin and the strip is then re-developed at right angles to the first direction. *One-dimensional procedure on filter-paper*—Apply the sugars (1 to 150 μg) to the paper and spray with a 2 per cent. soln. of ninhydrin in 95 per cent. ethanol containing 4 per cent. of pyridine. Hang the paper at 80°C for 3 hr. in a closed vessel containing, at the bottom, 50 per cent. aq. pyridine. Chromatograph by the descending technique with butanol - ethanol - water (4:1:1) and make the spots visible by a modification of the silver oxide reduction procedure described by Trevelyan *et al.* (*Brit. Abstr. C*, 1951, 260). W. H. C. Shaw

421. **The rapid identification of bile acids with an antimony trichloride colour reagent.** J. B. Carey and H. S. Bloch (*J. Lab. Clin. Med.*, 1954, **44** [3], 486–489).—A saturated soln. of $SbCl_3$ in $CHCl_3$ is recommended in a spot test for the identification and approx. determination of 5 to 80-μg amounts of 12 bile acids. Filter-paper carrying the sample spots is dried for 4 min. at 90°C, rapidly dipped in $SbCl_3$ reagent and re-dried for 4½ min. The fluorescence colours produced (observed in u.v. radiation) are specific for the position and number of hydroxyl or oxo groups attached to the cholanic acid nucleus. Amino or ethyl groups attached to the side-chain carboxyl group do not alter the fluorescence appreciably. W. H. C. Shaw

422. **Bacterial β-glucuronidase as a reagent for the hydrolysis of urinary corticosteroids.** B. N. Horwitt (*J. Lab. Clin. Med.*, 1954, **44** [3], 478–485).—The rapid procedure described requires the use of bacterial β-glucuronidase for the enzymic hydrolysis of urinary corticosteroid conjugates, which are mainly glucuronides. The liberated steroids are determined by the formaldehydogenic method of Corcoran and Page (*J. Lab. Clin. Med.*, 1948, **33**, 1326) and by the Porter - Silber phenylhydrazine - H_2SO_4 method (*Brit. Abstr. C*, 1951, 215). *Procedure for hydrolysis and extraction*—Adjust 25 ml of urine to pH 7·0 with 2 *N* NaOH or conc. HCl. Add 5 ml of 0·3 *M* phosphate buffer (pH 7·0), 1 ml of water containing 500 units* of bacterial β-glucuronidase and 5 ml of $CHCl_3$. Incubate at 38°C for 20 to 24 hr., cool and adjust to pH 1·0 with conc. HCl. Extract four times with 25-ml quantities of $CHCl_3$, combine the extracts, clarify with anhydrous Na_2SO_4 and filter. Wash the filtrate by shaking with two 12-ml portions of 0·1 *N* NaOH and then with 12 ml of water. Combine the aq. washings and extract with 25 ml of $CHCl_3$. Combine the $CHCl_3$ extracts, remove water with anhydrous Na_2SO_4 and evaporate to dryness *in vacuo* at < 45°C. [*One unit of enzyme activity liberates 1 μg of phenolphthalein from 3 to 5 $\times$ 10^{-4} *M* phenolphthalein glucuronide at pH 6·0 in 0·05 *M* acetate buffer in 1 hr. at 37°C.] W. H. C. Shaw

423. **Chromogenic values of various ketosteroids in a micro modification of the Zimmermann reaction: comparison with the macro procedure.** H. Wilson (*Arch. Biochem. Biophys.*, 1954, **52** [1], 217–235).—A micro modification of the macro Zimmermann method of Callow *et al.* (*Biochem. J.*, 1938, **32**, 1312) requires a reaction temperature of 0° C, increased KOH concn. and a reduced final vol. A detailed comparison is made between the macro and the proposed micro modification in respect of rate of colour development, wavelength of max. absorption, visible colour and sensitivity for a series of twenty-three 17-ketosteroids, four 3-monoketosteroids, nine 20-ketosteroids of the pregnane and *allo*pregnane series and seven corticosteroids. The proposed

micro method, which is suitable for use with chromatographic eluates, is sensitive to 2 μg of 17-ketosteroids and gives with, for example, dehydro-*iso*androsterone a rectilinear calibration between 2 and 40 μg with a standard error (triplicate determinations) of 2 per cent. The behaviours of different classes of steroids in both the micro and macro procedures are discussed in detail. *Procedure*—Make up all components of the reaction mixture in absolute ethanol. Transfer exactly 0·1 ml of ethanol (for blank), of 17-ketosteroid solution (for standardisation) or of test solution to a 10 × 75-mm Pyrex-glass tube and add 0·1 ml of 2 per cent. *m*-dinitrobenzene. Place the tube in an ice - salt bath at 0° C and allow to cool to 0° C. Add 0·2 ml of 2·5 *N* KOH (in ethanol and stabilised with ascorbic acid and N) and immediately mix by shaking (avoid bright light after adding KOH). Stopper the tube, replace it in the ice bath and keep in a refrigerator at 0° C for 3 hr. Add 0·5 ml of 80 per cent. ethanol, mix and measure the absorption at 530 mμ on a Coleman spectrophotometer fitted with adaptor and shield covering the meniscus. W. H. C. SHAW

424. **Chromatography of iodine-131 labelled esters.** W. M. Stokes, F. C. Hickey, O. P. Fish and W. A. Fish (*J. Amer. Chem. Soc.*, 1954, **76** [20], 5174–5175).—The separation by chromatography of the ^{131}I-labelled *p*-iodobenzoates of the sterols is described; the esters of cholestanol, cholesterol and 7-dehydrocholesterol are separated on a 60-cm column in 16 hr. and have m.p. of 186°, 184·5° and 178·5°C, respectively. Quantitative estimation of the content of a zone is simultaneous with its localisation, so permitting the analysis of any alcohol mixtures whose esters can be formed in high yields. D. BAILEY

425. **Studies on follicular hormones. VI. Quantitative analysis of oestrone and oestradiol by paper chromatography and measuring the area of coloured spot.** Einosuke Koshimura and Seiichi Okazaki (*Pharm. Bull., Japan*, 1954, **2** [1], 65–69).—After developing oestrone and oestradiol with benzene saturated with 10 per cent. NaOH on the alumina-impregnated filter-paper, and spraying iodine-saturated light petroleum reagent on to it, areas of the coloured spots of oestrone and oestradiol were measured. The min. detectable amount of oestrone was 2·5 μg, and of oestradiol 1·25 μg. A straight-line relationship was observed between the logarithm of amount of steroid and area of its spot. From this result, by the four-point assay or locating the area of steroids on the standard curve of oestrone and oestradiol, both steroids were quantitatively analysed simultaneously; this method was applied to the crude benzene extract from hydrolysed pregnant mare's urine. The result showed that the benzene extract contained about 56 per cent. of oestrone and 10 per cent. of oestradiol. O. M. WHITTON

426. **Phylloquinone reductase. (Preliminary communication.)** C. Martius and R. Strufe (*Biochem. Z.*, 1954, **326** [1], 24–25).—The activity of phylloquinone (Vitamin K_1) reductase is determined by measurement of the production of the reduced form of diphosphopyridine nucleotide (absorption at 366 mμ) in the following system: 3 × 10^{-4} *M* diphosphopyridine nucleotide (0·1 ml) - 5 × 10^{-4} *M* vitamin K_1 (0·1 ml) - phosphate buffer (0·2 ml) - enzyme suspension (0·1 ml). Tween 80 is used to bring vitamin K_1 into aq. soln.
G. W. CAMBRIDGE

427. **Aromatic biosynthesis. XIII. Conversion of quinic acid to 5-dehydroquinic acid by quinic dehydrogenase.** Susumu Mitsuhashi and B. D. Davis (*Biochim. Biophys Acta*, 1954, **15** [2], 269–280).—Quinic acid dehydrogenase can be assayed spectrophotometrically by following the increase in absorption at 340 mμ due to the formation of the reduced form of diphosphopyridine nucleotide in the following system: quinic acid (10 micromoles), diphosphopyridine nucleotide (1 micromole), potassium carbonate - bicarbonate buffer (pH 9·4) (100 micromoles), in a total volume of 3 ml in a silica cell. In certain crude preparations, dehydroquinic acid formed in the reaction was converted to shikimic acid, this being a coupled reaction with the reduced form of the diphosphopyridine nucleotide, so interfering with the assay. A method of bio-assay of such preparations for quinic dehydrogenase activity is described. G. W. CAMBRIDGE

428. **The activity of serum aldolase in progressive muscular dystrophy (Erb).** W. Jacob and J. Neuhaus (*Klin. Wochschr.*, 1954, **32** [37–38], 923–924).—The method proposed for the estimation of serum aldolase is based on the formation of triose phosphate from hexose diphosphate (**I**) and subsequent formation of its 2:4-dinitrophenylosazone or dihydrazone, which forms a red colour in alkaline solution and can be estimated spectrophotometrically at 540 mμ. Serum (1·0 ml) is treated with 0·1 *M* collidine buffer at pH 7·4 (1 ml), 0·56 *M* hydrazine soln. at pH 7·4 (0·25 ml), 0·002 *M* iodoacetate soln. at pH 7·4 (0·25 ml), distilled H_2O (0·25 ml) and 0·06 *M* **I** soln. at pH 7·4 (0·25 ml). After incubation for 1 hr. at 37° C, 10 per cent. aq. trichloroacetic acid (3 ml) is added. After filtration, 1·0 ml of the filtrate is treated with 0·75 *N* NaOH (1 ml). After standing the solution at room temperature for 10 min., 2:4-dinitrophenylhydrazine (1 ml) is added and the mixture is incubated for 10 min. at 37° C. The mixture is then made up to 10 ml with 0·75 *N* NaOH and the red colour is estimated in a step photometer (filter S53) or in a spectrophotometer at 540 mμ. Blank determinations are carried out, the **I** being added after the removal of the protein. The estimation of the colour must be carried out within 3 to 15 min. of its development. Haemolysis of the blood must be avoided since red cells contain large amounts of aldolase. The activity is expressed as cu. mm of **I** split by 1 ml of serum under the standard conditions. G. W. CAMBRIDGE

429. **Enzymic micro-determination of succinate and fumarate in tissue homogenates.** C. Bril (*Biochim. Biophys. Acta*, 1954, **15** [2], 258–262).—Succinic acid in ether extracts of suitably deproteinised homogenates can be determined by the action of succinic acid dehydrogenase (derived from rat-liver homogenate) with 2:3:5-triphenyltetrazolium chloride (TTC) as electron receptor. The latter forms the red acetone-sol. formazan, which can be determined spectrophotometrically, a linear relation existing between extinction and succinate concn. over the range 0 to 150 μg. Fumarate is determined after reduction to succinate by zinc dust and phosphoric acid. The homogenate is deproteinised by adding one-fifth of its volume of 5 per cent. metaphosphoric acid (no shift of the succinate - fumarate equilibrium occurs under these conditions). After centrifugation, a 9-ml sample is taken and treated with 10 *M* H_3PO_4 (1 ml), pentanol (1 drop) and 20 per cent. $CuSO_4$ soln. (1 drop). Reduction is induced by the addition of 300 mg of zinc dust and the mixture is filtered and extracted

with ether. A 10-ml sample of the deproteinised homogenate is also extracted with ether. The extraction is carried out in a cold-finger type of extractor; 500 μg of succinate can be quantitatively extracted with 25 ml of ether within 2 hr. if 10 ml of ether pass the soln. per min. The non-reduced extracts are treated with 0·05 *M* phosphate buffer, pH 6·8 (1 ml), the reduced extracts with 0·05 *M* Na_2HPO_4 soln. (1 ml) and the ether is evaporated. The aq. residues are transferred to measuring cylinders with 0·1 *M* phosphate buffer and made up to a suitable volume. One-ml aliquots are used for the determination of succinate. Into 15-ml tubes are put by pipette 1 ml of succinate soln., 1 ml of 0·5 per cent. TTC soln. in 0·1 *M* phosphate buffer and 1 ml of freshly prepared succinic acid dehydrogenase suspension, and the mixture is incubated at 37° C for 20 min. The reaction is then stopped by adding 5 ml of acetone and the tubes are stoppered and cooled in ice. After shaking and then centrifuging, the optical densities of the red supernatant liquids are determined at 480 mμ, a blank correction being applied. Amounts of both acids from $\simeq$ 10 μg upwards can be determined with an accuracy of $\pm$ 5 per cent.

G. W. CAMBRIDGE

430. **The determination of fructose 6-phosphate and fructose 1:6-diphosphate.** J. H. Roe and N. M. Papadopoulos (*J. Biol. Chem.*, 1954, **210** [2], 703–707).—The colorimetric method of Roe (*Brit. Abstr. A*, 1934, 1379) for the determination of fructose is modified for the determination of fructose 6-phosphate and fructose 1:6-diphosphate in the presence of each other and of other carbohydrates. The two esters are separated from a trichloroacetic acid tissue extract, at pH 8·3, by conversion into the Ba salts; the Ba salt of the diphosphate separates from the aq. solution and the Ba salt of the monophosphate is pptd. from the filtrate by addition of 4 vol. of ethanol. The phosphate groups are then hydrolysed off. In the proposed method, the concn. of HCl is increased, the reaction mixture is kept at 80° C for 13 min., and acetic acid, instead of ethanol, is used as solvent for the resorcinol in the Seliwanoff colour reaction. Conditions are adjusted to allow the use of free fructose as the reference standard. Interference by glucose 6-phosphate can be eliminated by oxidation of the glucose with Br to gluconic acid. The optical density of the colour produced in the Seliwanoff reaction is determined colorimetrically with a 515-mμ filter.

J. N. ASHLEY

431. **A quantitative method for the micro-estimation of phenylpyruvic acid.** W. Keup (*Biochem. Z.*, 1954, **326** [1], 14–17).—A method is described for the paper-chromatographic separation of phenylpyruvic acid and its estimation, after elution from the paper, by a colour reaction with ferric chloride in acid soln. Urine (0·1 ml) is placed on the paper which is rolled into a cylinder and stitched together (not metal clips). The chromatogram is run in acetic acid - H_2O (1 + 1) containing 0·01 ml of 2 *N* $FeCl_3$ soln. in 10 litres. After 3 hr., the paper is dried and examined. Staining of the phenylpyruvic acid with the ferric chloride indicates the area to be eluted. If the amount of phenylpyruvic acid present is unknown, larger amounts of urine may be run on the paper and the area localised by spraying with 0·2 *N* $FeCl_3$ and the corresponding area on a duplicate paper can be eluted. Elution is carried out in ethanol (total volume 6 ml), and 4 ml of the eluate are treated with 1 ml of ferric chloride reagent [2 *N* $FeCl_3$ (0·1 ml), Sorensen's glycine buffer, pH 1·7 (10 ml)]. After exactly 1 min., the colour is determined on a spectrophotometer at 600 mμ or on a step photometer with an S 61 filter. A blank with ethanol and reagent is also examined and the phenylpyruvic acid is determined by reference to a calibration curve, linear over the range 0 to 1·0 per cent.

G. W. CAMBRIDGE

432. **Remarks on Roman's method for determining choline.** L. Acker and H. Bücking (*Z. anal. Chem.*, 1954, **143** [5], 352–353).—Low results obtained in determining choline by Roman's method (pptn. of choline by KI_3 and titration of the complexed iodine) are attributed to only 8 of the 9 I in choline enneaiodide being titratable by $Na_2S_2O_3$. This new factor increases precision to $\pm$ 1·4 per cent.

D. R. GLASSON

433. **Assay of histamine on the isolated guinea-pig intestine by the method of superfusion.** H. M. Adam, D. C. Hardwick and K. E. V. Spencer (*Brit. J. Pharmacol.*, 1954, **9** [3], 360).—A method is described for the estimation of minute quantities of histamine (1 to 5 μg per ml.) A piece of guinea-pig ileum 3 to 4 cm long is suspended in a constant flow of a modified Tyrode-Ringen solution containing 0·1 μg per ml of atropine. Tension is applied for 30 min. by applying weights to the lever. Doses of histamine are then given at 90-sec. intervals, from a semi-automatic apparatus, until the gut becomes sensitive and gives regular responses (average 32 doses). The assay is then begun using the (2 + 2) dose design described by Schild. For 12 assays the mean λ value was 0·030 (range 0·012 to 0·052). Several assays can be carried out on the same preparation. Dilutions of the histamine solutions are made in Tyrode solution. Hypotonic Tyrode solutions, or solutions containing an excess of KCl or $CaCl_2$, are slightly active.

G. F. SOMERS

434. **Analysis of high molecular weight alcohols by the mass spectrometer. The wax alcohols of human-hair fat.** R. A. Brown, W. S. Young and N. Nicolaides (*Anal. Chem.*, 1954, **26** [10], 1653–1654).—High molecular wt. alcohols, separated as a fraction from human-hair fat, were analysed by high-temp. mass spectrometry. To interpret results calibration spectra were taken of C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{24}, C_{28}, C_{29}, C_{30}, C_{31}, C_{32}, C_{33} and C_{34} normal alcohols as well as of oleyl alcohol. Other alcohols known to exist in wool wax were also examined. Two homologous series were identified in the fat, an aliphatic one ranging from C_{16} to C_{27} and the mono-olefinic series ranging from C_{18} to C_{27}. Alcohols having an even number of C atoms are present in significantly greater quantity than adjacent ones with odd numbers.

G. P. COOK

See also Abstracts 273, 279, 299, 320, 331, 347, 379, 445.

Drugs

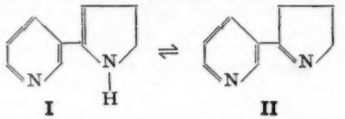
435. **A new partition chromatographic procedure for the assay of pharmaceuticals.** D. Banes (*J. Amer. Pharm. Ass., Sci. Ed.*, 1954, **43** [10], 580–584).—A new procedure for the assay of pharmaceuticals is described. The sample is incorporated with an immobile solvent and a supporting medium (Celite) to form a column suitable for chromatographic development; the therapeutic substances are then isolated by differential elution. Details are presented for the rapid assay of digitoxin in tablets, the quantitative separation of strychnine and quinine, and the analysis of mixtures containing

acetylsalicylic acid, phenacetin and caffeine. The method has been employed in the assay of oestrogenic preparations, barbiturates, cardioactive glycosides and mixed sulphonamides.

O. M. WHITTON

436. **Examination of medicines by means of fluorescence analysis.** F. Köchel (*Dtsch. ApothZtg.*, 1954, **94** [45], 1095–1097).—This review of the factors affecting fluorescence, and of the techniques used on the micro scale, has particular reference to homoeopathic medicines. A. R. ROGERS

437. **Infra-red spectra of nicotine and some of its derivatives.** C. R. Eddy and A. Eisner (*Anal. Chem.*, 1954, **26** [9], 1428–1431).—Nicotine and five related alkaloids (dihydrometanicotine metanicotine, myosmine, nicotyrine and nornicotine) can be identified by their infra-red spectra (which are reproduced) even when they have identical u.v. spectra. The absence of a band near 3300 κ (Kayser) in myosmine suggests the absence of an N–H bond, whilst the presence of a band at 1621 κ suggests a C=N linkage, rather than a C=C one in the 5-membered ring. If myosmine exists as two tautomers, then the infra-red spectrum gives evidence in favour of **II**, rather than of the accepted structure **I**.



I **II**

J. H. WATON

438. **The separation of ergot alkaloids by paper chromatography.** M. Pöhm and L. Fuchs (*Naturwissenschaften*, 1954, **41** [3], 63).—The method allows a complete separation of laevo- and dextro-rotatory alkaloids, whether derived from raw or purified preparations. Whatman No. 1 paper is impregnated with formamide containing 4 per cent. of benzoic acid; the optimum amount of formamide is 0·5 g per sq. dm. The developer consists of a mixture of carbon tetrachloride, chloroform and benzene (7:2:1) and the descending technique is used. Ergometrine and ergometrinine remain at the point of application, but can be resolved further by the method of Foster, Macdonald and Jones (*J. Pharm. Pharmacol.*, 1949, **1**, 802). Next in order of speed of migration are ergotamine, ergosine, ergotaminine, ergosinine, ergocristine and ergocornine, ergocryptine, ergocristinine and ergocorninine, and, finally, erogcryptinine. The alkaloids are recognised by their intense fluorescence in u.v. light. The chromatograms are suitable for quantitative evaluation. E. KAWERAU

439. **Sabadilla alkaloids. IV. Separation of veratridine and cevadine by partition chromatography.** G. R. Svoboda and L. M. Parks (*J. Amer. Pharm. Ass., Sci. Ed.*, 1954, **43** [10], 584–588).—Veratridine and cevadine, respectively, have been separated in a high state of purity from prepared mixtures of the known alkaloids, from commercial veratrine and from the mixture of alkaloids obtained by extraction of sabadilla seed with Skellysolve B by partition chromatography on a silicic acid column buffered at pH 4·00 and 4·25 and with $CHCl_3$ as the eluting solvent. Experimental details are given. O. M. WHITTON

440. **Analysis of mixtures of theobromine and caffeine by spectrophotometric method.** J. W. Miles and D. T. Englis (*J. Amer. Pharm. Ass., Sci. Ed.*, 1954, **43** [10], 589–592).—The u.v. absorption characteristics of theobromine and caffeine in both acidic and alkaline solutions have been investigated. Methods have been developed for the simultaneous determination of the two constituents in mixtures containing up to 30 mg per litre of the two alkaloids. The reliability of the working-curve method depends mainly upon the magnitude of the difference between the absorbancy of the theobromine in alkaline and acid solutions at 240 mμ; in the simultaneous-equation method, it depends mainly upon the difference between the absorption of the theobromine and caffeine when both are examined in alkaline solution at 240 mμ. Results for representative analyses of mixtures, in which the quantities of the two constituents are varied within a total of 30 mg per litre are given. The average error is ± 1·0 per cent. by calibration curves and ± 1·6 per cent. by the simultaneous equations. O. M. WHITTON

441. **The assay of digoxin preparations.** D. Banes (*J. Amer. Pharm. Ass., Sci Ed.*, 1954, **43** [6], 355–357).—An improved method is described for the colorimetric determination of digoxin (**I**) with *m*-dinitrobenzene in weakly alkaline solution. As the alkali concentration is critical, interfering acidic substances must be removed first. *Injections*—A volume of solution containing ≃ 2·5 mg of **I** added to 50 ml of 10 per cent. Na_2SO_4 solution and 2 ml of *N* HCl is extracted with seven 25-ml portions of $CHCl_3$, each extract being washed with the same 10 ml of water and filtered through a cotton-wool pledget. The combined extracts are evaporated to dryness, the residue is dissolved in hot alcohol, and the solution is diluted to 50 ml with alcohol. *Tablets*—A quantity of powdered tablets equivalent to ≃ 2·5 mg of **I** is boiled gently for 20 min. with 20 ml of alcohol and transferred to a separator with three 10-ml portions of alcohol and 50 ml of water. The mixture is cooled, acidified with 1 ml of *N* HCl and extracted immediately with two 50-ml portions of *iso*octane, the combined extracts being washed with 20 ml of 50 per cent. alcohol and two 20-ml portions of water. The combined extracted aqueous liquid and the washings are diluted to 400 ml with 10 per cent. w/v sodium sulphate soln. and extracted with $CHCl_3$ as described for injections. *Determination*—A 5-ml aliquot of the prepared alcoholic solution is evaporated to dryness, cooled *in vacuo* for 30 min., and 4 ml of freshly prepared *m*-dinitrobenzene reagent (1·6 g are dissolved in 80 ml of hot alcohol, the mixture is cooled, 1 ml of a 10 per cent. aq. soln. of tetramethylammonium hydroxide are added, and the solution is diluted to 100 ml with alcohol) are added. After 15 min. at room temp., the intensity of the blue-violet colour is measured at 615 mμ against a reagent blank until a max. is reached. The amount of **I** present is derived by comparison of the colour with that given by a 5-ml aliquot of a standard solution containing 50 μg of **I** per ml. Under these conditions up to 8 per cent. of gitoxin (**II**) does not seriously affect the accuracy of the method. A colorimetric method is also described for the determination of **II** in the presence of **I**, based on the conversion of **II** to dianhydrogitoxigenin, followed by chromatographic separation and estimation with Windaus - Schwarte reagent.

S. C. JOLLY

442. **The biological assay of adrenaline with the hexamethonium-treated cat.** G. F. Somers (*Analyst*, 1954, **79**, 627–629).—A method is described for the

assay of adrenaline by means of the hexamethonium-treated cat. Hexamethonium, a potent hypotensive drug, blocks the sympathetic and parasympathetic ganglia and thus provides a simple alternative procedure to "spinalising." Hexamethonium bromide is injected subcutaneously into the anaesthetised cat, and the blood pressure, recorded from the carotid artery, is allowed to fall to a steady base value. Injections of standard adrenaline soln. are made into the femoral vein and the responses are recorded. Similar doses of the test soln. are injected according to a statistically valid pattern and the potency is then assessed. Results compare favourably with those by other methods.

A. O. JONES

443. **An application of the "up and down method" for insulin assay.** Y. Ito, B. Tamaoki and K. Kurata (*Pharm. Bull. Japan*, 1954, **2** [3], 234).—The "up and down method" has been applied to the mouse method of insulin assay and results have been compared with the standard probit method. The principle of the method (see D. J. Finney, "Probit Analysis" 2nd Ed., 1952, Cambridge University Press, England) is to choose a logarithmic series of doses and to inject a mouse with one of these doses. If it responds another mouse is injected at the next lower dose, but if it does not respond the next higher dose is chosen, and so on with subsequent mice. This has the advantages of arithmetical simplicity, better efficiency and constant existence of estimate, even in small samples. The method is best suited for quick responses and was first introduced for testing the sensitivity of explosives to shock. For insulin assays it is extremely time-consuming. Two experiments are described and computed by this new procedure. The results compared well with the standard probit method. G. F. SOMERS

444. **The bio-assay of insulin *in vitro* by manometric measurements on slices of mammary glands.** J. D. Balmain, C. P. Cox, S. J. Folley and M. L. McNaught (*J. Endocrinology*, 1954, **11** [3], 269–276).—The addition of insulin increases the rate of lipogenesis and the respiratory quotient of rat-mammary slices *in vitro*. The metabolic responses of the mammary tissue can be used for the assay of insulin by standard manometric techniques. Abdominal mammary tissue from hooded Norwegian rats, killed by neck dislocation at the 12th to 15th day of lactation, is sliced with a microtome; 150 mg of the wet slices are incubated at 37° C in 3·0 ml of medium in Warburg flasks in an oxygen atmosphere containing 5 per cent. of CO_2. After gassing for 10 min., the supply is disconnected and the stoppers are closed. The pressure in the flasks is reduced, by a tightly fitting teat attached to the tap inlet to bring the level of manometer fluid in the open arm near the bottom of the scale when the level in the closed arm is on the fixed mark in the middle. The respirometers are then allowed to equilibrate for 5 to 10 min. and readings are then made over 3 to 4 hr. The net gas output is calculated as μl of CO_2 per mg of final dry weight. The medium is prepared by the addition of substrates, glucose (0·3 per cent.) and sodium acetate (0·02 *M*) to Krebs' bicarbonate - saline solution. Stock solutions of crystalline insulin are prepared by dissolving in a minimal quantity of 0·01 *N* NaOH and adding water to give a concn. of 100 μg per ml. Required concentrations of insulin are produced by serial dilution. The net gas output increased with the insulin concn. between 0·1 μg per ml and 2·5 μg per ml. The best response metameter was the logarithm of the pressure increase, as μl of CO_2 per mg final dry weight from 30 to 150 min. ($\log_{10} P_{30}^{150}$), against the logarithm of insulin concn. A six-point assay with concn. of 0·5, 1·0 and 2·0 μg per ml of insulin, with tissue from one rat and duplicate observations of P_{30}^{150}, when repeated for eight rats, gave a ratio of t to s of 0·9 with 5 per cent. fiducial limits of 0·76 and 1·07 (84 and 119 per cent). This compares favourably with 0·99 (0·9 and 1·09) obtained by standard assay procedures. The value of λ was 0·18 compared with 0·16 for the rabbit blood-sugar method. A six-point assay gives acceptable precision with eight rats, but with 12 respirometers it occupies 8 days. A four-point assay and the use of more apparatus reduced the time. G. F. SOMERS

445. **The determination of inositol as the hexa-acetate.** F. J. Bandelin, H. E. Deane and R. E. Pankratz (*J. Amer. Pharm. Ass., Sci. Ed.*, 1954, **43** [10], 577–580).—A method for the determination of inositol by reaction with acetic anhydride, extraction of the inositol hexa-acetate formed with ethylene dichloride and gravimetric determination as the hexa-acetate is described. The method is applied to pure inositol and tablet mixtures free from sugars and other materials amenable to acetylation with accurate and reproducible results having a mean deviation of less than $\pm$ 0·05 per cent. Sugars are removed by fermentation; by-products of fermentation and other polar materials are removed by ion exchange. Other lipotropic agents, such as choline, betaine and methionine, and starch do not interfere. O. M. WHITTON

446. **Paper chromatography of some basic butanol-soluble antibiotics.** W. T. Sokolski, S. Ullman, H. Koffler and P. A. Tetrault (*Antibiot. & Chemother.*, 1954, **4** [10], 1057–1060).—Details are given of 11 solvent systems found useful for separating erythromycin, carbomycin, methymycin and an antibiotic produced by a proactinomycin-producing strain of *Nocardia gardneri* (ATCC 9604). The best separation by the descending technique was obtained with *n*-nonanol - CCl_4 - propionic acid (75:75:2). R_F values for each antibiotic with the various solvents are listed. W. H. C. SHAW

447. **A composite curve procedure for antibiotic assays.** N. F. Knowlden (*Antibiot. & Chemother.*, 1954, **4** [10], 1061–1067)—A time-saving modification of the F.D.A. standard curve assay is described. The average slope of the graph of inhibition zone diameter plotted against log. concn. is determined from at least 20 slope values, and a composite curve is drawn through a point representing the zone diameter given by a standard soln. of the antibiotic and with the determined average slope value. The potencies of unknown samples are calculated from the average observed zone diameters, corrected for the difference between the zone diameter given by a standard solution assayed at the same time and the value is used in constructing the composite curve. The use of a control chart to detect significant deviation in slope values is described. The procedure has been found applicable to polymixin B, bacitracin and neomycin assays.

W. H. C. SHAW

448. **Simultaneous determination of penicillin and penicilloic acid in fermentation samples by a colorimetric method.** S. C. Pan (*Anal. Chem.*, 1954, **26** [9], 1438–1444).—Penicillin and penicilloic

acid are separated from each other by extraction of the sample with *iso*butyl methyl ketone at two pH values. Penicillin (93 per cent.) is extracted at pH 5·5 or lower when the aq. phase is 80 per cent. saturated with $(NH_4)_2SO_4$; penicilloic acid (93 per cent.) is extracted when the pH of the aq. phase is lowered to below 3·0. The penicillin of the first extract is converted to penicilloic acid by treatment with 2 *N* NaOH at room temp. and determined after reduction of arsenomolybdic acid in the presence of a trace of $HgCl_2$ by measurement at 660 mμ of the molybdenum blue produced. The effects of impurities are eliminated by destruction of the penicilloic acid by heating the sample in acid solution and applying the colorimetric procedure for a "blank value." Recoveries of penicillin and penicilloic acid from various fermentation media were within ± 5 per cent. When calculated on the sum of the penicillin and penicilloic acid, the errors were within ± 2 per cent. G. P. Cook

449. **Determination of phenylacetic acid and phenylacetamides in samples from penicillin fermentations.** S. C. Pan and D. Perlman (*Anal. Chem.*, 1954, **26** [9], 1432–1438).—Phenylacetic acid is extracted quantitatively from penicillin fermentation soln. acidified with dil. H_2SO_4 (containing benzylpenicillin or its degradation products) with toluene. The extracted phenylacetic acid is then measured by the Kapeller - Adler procedure for the determination of phenylalanine, modified to determine phenylacetic acid. The precision of this modification is ± 3 per cent. and the limiting concn. is ≃ 0·05 mg per ml. Phenylacetamide and other neutral derivatives are separated from the fermentation soln. by extraction into $CHCl_3$ from alkaline soln. The extracted phenylacetamides are hydrolysed to phenylacetic acid and are determined by the above procedure. G. P. Cook

450. **Separation of Aureomycin from Terramycin by counter-current distribution and paper chromatography.** R. J. Hickey and W. F. Phillips (*Anal. Chem.*, 1954, **26**, 1640-1642).—Aureomycin (chlortetracycline) and Terramycin (oxytetracycline) can be resolved by counter-current distribution by using a *n*-butanol - aq. 0·01 *N* HCl system; this procedure can be utilised for quant. and qual. separations. For paper-chromatographic separation a solvent system consisting of glacial acetic acid, *n*-butanol and H_2O (25:50:25) is used, and two distinct oval zones of R_F 0·77 and 0·70 for Aureomycin and Terramycin, respectively, are obtained. Mixtures of the antibiotics containing as little as 1·5 μg of each in 2·5 μl of solution can be qualitatively separated. G. P. Cook

451. **Spectrophotometric determination of tetracycline, oxytetracycline and chlortetracycline.** R. Intonti and F. Cotta-Ramusino (*Ann. Chim., Roma*, 1954, **44** [7–8], 437–442).—Between 25 and 50 mg of the product are dissolved in about 50 ml of water, and the absorption of 2-ml aliquots of this is measured at 268 mμ after making 0·1 *N* in HCl, at 380 mμ after making 0·25 *N* in NaOH and at 440 mμ after heating for 5 min. in a bath of boiling water at an acidity of 2 *N* HCl. The quantities of each of the three antibiotics can be deduced by inserting the measured absorptions in the following three equations: E at 268 mμ = $379x + 352y + 372{\cdot}5z$; E at 380 mμ = $373x + 24y + 309z$; E at 440 mμ = $162x + 139{\cdot}5y - 4z$, where *x*, *y* and *z* are the concn. of tetra-, chlortetra-, and oxytetra-cyclines, respectively. R. C. Murray

452. **Paper-chromatographic identification of the actinomycins.** L. C. Vining and S. A. Waksman (*Science*, 1954, **120**, 389–390).—A mixture of di-*n*-butyl ether, ethyl acetate and 2 per cent. napthalene-2-sulphonic acid soln. (3:1:4) was the most suitable solvent system for ascending and circular techniques. Whatman No. 1 paper was dipped in the aq. phase and blotted on filter-paper and the samples of actinomycin were applied in acetone soln. The deep-red colour of the naphthalene-2-sulphonic acid salt facilitated detection of the zones. The results of applying the method to various samples of actinomycins are tabulated and discussed. H. F. W. Kirkpatrick

453. **Experiments on the standardisation of capsicum fruit and tincture of capsicum.** G. Schenk (*Dtsch. ApothZtg.*, 1954, **94** [40], 970–972).—Methods of standardising capsaicin-containing drugs are reviewed and a new chemical test for *Fructus Capsici* D.A.B. VI is proposed. *Procedure*—Macerate 2 g of drug with 20 g of ethanol for 24 hr. Pass 10 g of the clear macerate through a column (120 × 8 mm) of Al_2O_3 (neutral) containing 1 per cent. of activated carbon; wash the column with sufficient ethanol to make the eluate up to ≃ 50 ml. Evaporate the ethanol on a water-bath and make the cooled residue up to 5 ml in a calibrated test-tube with water-free acetone. In a similar tube place 1·75 ml of 1 per cent. vanillin soln. in the same solvent, and make up to 5 ml. To each of the tubes add 9 drops of conc. HCl and 0·1 g of ammonium vanadate, taking care that these reagents do not touch the sides of the tubes. The tubes are shaken or the contents are stirred, and when the solutions have cleared (≃ 30 sec.), the blue - green colours are compared by bright transmitted light. The colour of the test solution must not be lighter than that of the vanillin solution. The tincture is tested in the same way. E. Hayes

454. **Mechanism of diazo reaction of 4-aminosalicylic acid and *m*-aminophenol [and determination of the latter in the former].** M. J. H. Croonen (*Pharm. Weekbl.*, 1954, **89** [39–40], 673–689).—On making alkaline a diazotised mixture of 4-aminosalicylic acid (**I**) and *m*-aminophenol (**II**), coupling occurs, not between the diazonium deriv. of **II** and resorcylic acid (formed from **I**), but between a portion of the diazonium deriv. of **I** and resorcinol (formed from **II**). The following colorimetric method for the determination of **II** as an impurity in **I** is based on the observed high reactivity and instability of the diazonium deriv. of **I** in comparison with that of the same deriv. of **II**. *Procedure*—Two 1-ml portions of the solution to be tested are treated (in test tubes) at 0° C, each with *N* H_2SO_4 (1 ml) and aq. 1 per cent. $NaNO_2$, and kept at 0° C for 5 min. After addition to each tube of 1 ml of aq. 30 per cent. urea and keeping at 20° C for 15 min. (the diazonium deriv. of **I** is decomposed, whilst that of **II** remains intact), the mixture in one tube is treated directly with 4 *N* NaOH (0·5 ml), whilst the other portion is similarly treated after heating the tube in boiling water for 5 min. and then cooling. The difference between the colorimetric values at 470 mμ of the two solutions (both made up to 10 ml) gives a measure of the amount of **II** present in the sample of **I**. The detection of 0·01 per cent. of **II** is possible. P. S. Arup

455. **Ultra-violet absorption spectra of the hydrolysis products of diethylbarbituric acid [barbitone].** G. R. Jackson, jun., J. R. Weschler and R. L.

Dannley (*Anal. Chem.*, 1954, **26** [10], 1661–1662).—The u.v. spectra of the hydrolysis products of diethylbarbituric acid (barbitone) were determined to ascertain whether these products interfere with the spectrophotometric determination of barbitone by the method of Goldbaum (*Anal. Chem.*, 1952, **24**, 1604). The u.v. spectra show that all except α-ethylbutyrylurea and diethylmalonuric acid give an optical density $< 0{\cdot}03$; but these two compounds give considerable absorption at the shorter wavelengths in alkaline soln. The interference at the Goldbaum wavelength of 260 mμ is negligible.
G. P. Cook

456. **Method for the quantitative determination of glycerol trinitrate in tablets.** M. S. Shraĭber and B. A. Rubinshteĭn (*Aptechnoe Delo*, 1954, **3** [5], 46–47).—The glycerol trinitrate is reduced to ammonia, which is then distilled into an excess of $0{\cdot}1\ N\ H_2SO_4$. To 40 tablets (0·5 mg per tablet) in a 500-ml round-bottomed flask, add 100 ml of freshly boiled and cooled water and shake until the tablets are completely disintegrated; then add 20 ml of ethanol, 25 ml of 16 per cent. NaOH soln., 5 ml of 10 per cent. $CuSO_4$ soln. and 2 g of aluminium turnings. Connect to a Kjeldahl adaptor and a receiver containing 10 ml of $0{\cdot}1\ N\ H_2SO_4$ and a drop of methyl red in freshly boiled water. When the vigorous reaction has ceased, heat carefully. When the reaction is complete, titrate the excess of acid with $0{\cdot}1\ N$ NaOH. A control experiment is carried out at the same time. E. Hayes

457. **Ultra-violet irradiation and absorptiometric methods for the determination of stilboestrol in tablets.** J. M. Goodyear, L. S. Hatfield and M. M. Marsh (*J. Amer. Pharm. Ass., Sci. Ed.*, 1954, **43** [10], 605–608).—Two methods for the determination of stilboestrol in tablets are described. In the first method, the yellow colour developed on irradiating an aqueous acetic acid solution of the compound by u.v. light is used as a measure of concentration; the second method relates concentration to absorbancy differences of acid and alkaline solutions of diethylstilboestrol in the u.v. range. Results of studies of variables in the procedures and certain specific interferences are reported. Precision of the irradiation procedure is ± 1 per cent. and of the absorbancy difference procedure ± 1·5 per cent.
O. M. Whitton

458. **Determination of zinc oxide in calamine lotion.** M. Pernarowski and L. G. Chatten (*Drug Standards*, 1954, **22** [9–10], 181–184).—Measure 10 ml of calamine lotion in a 10-ml calibrated flask and transfer it completely with water to a filter-paper on a Buchner funnel. Wash the residue with water and transfer the filter-paper with the residue to a beaker. Add 50 ml of $N\ H_2SO_4$ soln., warm for a few min. and stir until no further solution occurs. Filter and wash the residue with hot water until the washings are neutral to litmus. Cool and make up to 250 ml with water. To a 50-ml aliquot, add 1·5 g of NH_4Cl and titrate with N NaOH, with methyl orange as indicator. N.E.

459. **Quantitative determination of sodium nitrite in pharmaceutical mixtures.** G. A. Vaĭsman (*Aptechnoe Delo*, 1954, **3** [5], 9–12).—Sodium nitrite is determined by titration with sulphanilamide. To 2 ml of $0{\cdot}1\ N$ sulphanilamide soln. (1·722 g of sulphanilamide dissolved in 10 ml of 25 per cent. HCl and made up to 100 ml with water) add 2 ml of 25 per cent. HCl. The $NaNO_2$ soln. is placed in a burette and run into the ice-cooled sulphanilamide soln. until a drop of the soln. gives an immediate blue colour with starch - iodide paper. The determination can be carried out without interference in the presence of tinctures or infusions of valerian; digitalis or adonis, theobromine, sodium salicylate, caffeine, sodium benzoate, phenobarbitone and extract of belladonna. E. Hayes

See also Abstracts 263, 276, 389, 414, 469, 471, 475, 479, 481.

Food

460. **Apparatus for the determination of small amounts of sulphur dioxide in food products by Grant's method.** J. Penasse and H. Cheftel (*Ann. Falsif.*, 1954, **47**, 345–346).—A convenient apparatus is described for use in the modification described by Dupaigne (*Ann. Falsif.*, 1951, **44**, 111) of Grant's method (*Brit. Abstr. C*, 1947, 214) for determining small amounts of SO_2 in food products.
S. C. Jolly

461. **Determination of inorganic constituents in sucrose solutions.** A. Gee, L. P. Domingues and V. R. Deitz (*Anal. Chem.*, 1954, **26** [9], 1487–1491).—Rapid procedures for the analysis of commercial sugars without ashing were investigated. Flame photometry was used to determine K, Na, Ca and Mg; the hydrogen flame gave the best results when 5° Brix solutions were used. An alternative procedure for total Ca and Mg involved titration with ethylenediaminetetra-acetic acid at pH 10, with Eriochrome black T as indicator. The Ca content was found by titration at a pH > 12 with murexide as indicator. Results for Ca and Mg by titration and photometry agreed closely. Phosphate and silicate determinations were carried out by the molybdenum-blue method, and chloride determinations by conductimetric titration with $AgNO_3$. The SO_4'' content was determined by pptn. with $BaCl_2$ and measurement of the turbidity produced by either transmitted or scattered light. The precision of the colorimetric and turbidimetric methods was ± 5 per cent., for the titrations ± 1 to 2 per cent. and for the photometric methods ± 1 to 5 per cent. The procedures were tested on one raw sugar only.
G. P. Cook

462. **Photometric determination of glucose in the presence of fructose.** F. Stitt, S. Friedlander, H. J. Lewis and F. E. Young (*Anal. Chem.*, 1954, **26** [9], 1478–1483).—The method is based on the fact that $NaClO_2$ soln. at pH 4·0 oxidises glucose more rapidly than fructose. The ClO_2 produced is measured spectrophotometrically or colorimetrically by its absorption at ≃ 436 mμ. The difference in ClO_2 produced by oxidation of the sample and of a suitable reference fructose sample gives a measure of the glucose content. The concn. range is 0·05 to 0·5 per cent. of glucose in fructose. In samples containing $< 0{\cdot}5$ per cent. of glucose percentage standard deviations of ± 0·003 are obtained; for samples containing 0·5 to 5·0 per cent. of glucose ± 0·3; and for samples $> 5{\cdot}0$ per cent of glucose ± 1. Standard deviations for the colorimetric procedure are greater by a factor of 1·5 to 2·0.
G. P. Cook

463. **Statistical analysis of differences between refractometric readings and analysis of sugar in sugar-beet juice, and the influence of varietal differences and degree of maturity.** J. R. Pasalacqua (Ministry of Industry and Commerce, National Energy Enterprises, Vegetable Fuels and Derivatives, Buenos Aires, 1953, 10 pp.).—The difference between results for sugar content calculated from

refractometric readings and from chemical analysis in sugar-beet juice has been studied statistically. A factor relating refractometric determinations made in the field to the true values given by chemical methods in the laboratory is deduced. Soil and beet variety do not influence the relationship noticeably. H. PRITCHARD

464. **Spanish dried apricots.** R. Casares and C. Lopez Herrera (*An. Bromatologia*, 1954, **6** [2], 165–171).—Methods used for the analysis of dried apricots are outlined and results on 3 samples of apricots of Spanish origin are reported. L. A. O'NEILL

465. **Application of paper microchromatography to the study of organic acids in jams.** R.-I. Cheftel (*Ann. Falsif.*, 1954, **47** [7–8], 281–284).—Jam (150 g) is mixed with 250 ml of ethanol, kept for 48 hr., filtered and diluted to 300 ml. A 100-ml portion of this solution is then mixed with distilled water and passed through a column of De-Acidite E, which retains the acids. The acids are then eluted with ten 10-ml portions of *N* aq. NH_3 soln. and ten 30-ml portions of water, and the eluate is evaporated to 10 ml. The NH_4^+ salts are converted to free acid (by acidification with H_2SO_4 or ion exchange) and paper-chromatographed with a solvent of *n*-propanol - cineole - formic acid (50:50:20 by vol.) saturated with H_2O (Cheftel *et al.*, *Bull. Soc. Chim. Biol.*, 1951, **33**, 840–845). The presence of apple in strawberry jam is indicated by the appearance of a spot for malic acid, of which strawberries contain very little. Apricots contain malic acid and citric acid, but the presence of apple is shown by a change in the relative amounts of these acids; owing to the variability of the citric acid content of apricots with ripeness, the method is only reliable when a sample of the same jam unadulterated or the original apricot pulp is available. E. J. H. BIRCH

466. **Volumetric determination of pectin as calcium pectate.** R. Holt (*Analyst*, 1954, **79**, 623–627).—A method is described for the direct determination of the Ca content of pptd. Ca pectate by titration with ethylenediaminetetra-acetate soln. (**I**). The sample soln. (< 200 ml containing 30 to 120 mg of pectin calculated as Ca pectate) is treated with 0·5 *N* NaOH and, after 5 min., with 50 ml of *N* acetic acid. The vol. is then adjusted to 350 ml with water and 50 ml of *M* $CaCl_2$ are run into the vigorously stirred liquid. After 10 min., the liquid is boiled and filtered, and the filter is washed with boiling water. The ppt. is then suspended in water and boiled and re-filtered through the same paper. After further washing to remove all Cl′, the ppt. is suspended in water, treated with a buffer soln. ($Na_2B_4O_7$, NaOH and Na_2S) and an excess of **I** (prep. described). The liquid is raised to the b.p. and shaken until the ppt. dissolves. After partial cooling, the excess of **I** is back-titrated with standard $CaCl_2$ soln., with Eriochrome black T as indicator. Pectate ions do not interfere. A. O. JONES

467. **Apparatus for the aseptic removal for analysis of the gas contained in a can of conserves.** G. Thomas and H. Cheftel (*Ann. Falsif.*, 1954, **47**, 347–349).—A small apparatus is described which enables gas to be withdrawn from a can and replaced by sterile air without contamination of the contents. S. C. JOLLY

468. **Spanish rice.** J. Oca (*An. Bromatologia*, 1954, **6** [2], 107–113).—Methods for the analysis of rice are outlined; results of analyses on some Spanish varieties are reported. L. A. O'NEILL

469. **Biological detection of antiseptics and antibiotics in milk.** J. Pien, J. Lignac and P. Claude (*Chim. et Ind.*, 1954, **72** [1], 51–58).—Curdling inhibitors in milk are detected by incubating a sample at 30°C with a known amount of a lactic ferment, and comparing the rate of production of lactic acid with that of a similarly treated sample of authentic unpreserved milk. A 20 per cent. reduction in the amount of lactic acid produced, especially in the early stages of the fermentation, indicates the presence of an inhibitor. Natural inhibitors are distinguished from artificial additives by carrying out the test on a sample heated to 95°C for 30 sec.; this treatment destroys natural, but not artificial, inhibitors. If an antiseptic or antibiotic is present, it can be identified by the use of a series of strains of *Streptococcus lactis*, each strain being made resistant to one particular antiseptic or antibiotic; the milk sample is incubated with cultures of the different strains, and production of lactic acid is greatest with the strain corresponding to the inhibitor present. By the use of strains resistant to varying concn. of antibiotic or antiseptic, the amount present in the sample can be determined. E. HAYES

470. **Spanish vegetables.** R. Casares and M. T. Valdehita (*An. Bromatologia*, 1954, **6** [2], 115–144).—Methods used for the analysis of vegetables are outlined and results are reported for 39 different types. L. A. O'NEILL

471. **Microbiological method for detecting antiseptics and antibiotics in bottled beers.** D. A. A. Mossel (*Ann. Falsif*, 1954, **47**, 349–357).—A fermentation method is described for the detection of antiseptics and antibiotics in beer. *Procedure*—To ≃ 100 ml of beer introduced aseptically into a sterile 250-ml flask, a sterile 50 per cent. glucose solution (5 vol. per 100 vol.) and a concentrated nutrient solution, sterilised by filtration, are added. The mixture is degassed by agitating the flask, inoculating with 1 ml of a dilution of bakers' yeast in 0·85 per cent. NaCl solution containing ≃ 10^4 cells per ml, shaking vigorously, and adding 2 Einhorn tubes immediately. After 68 to 72 hr. at 25° C, the volume of gas in the tubes is measured. The following min. levels, in parts per 100, are reported to cause a 50 per cent. reduction in gas production: cetyltrimethylammonium bromide 5×10^{-4}, ethyl bromoacetate 2×10^{-5}, phenylmercury salts 3×10^{-5} to 10×10^{-5} and Actidione 10^{-5}. S. C. JOLLY

472. **Detection of traces of artificial colours in wine.** E. Portal and J. Bonastre (*Ann. Falsif.*, 1954, **47**, 341–345).—An improved method is described for the detection and estimation of artificial colours in wine. *Procedures*—The wine (≃ 200 ml) is evaporated to one-third of its volume, dil. (1 + 10) HCl (3 ml) and bleached wool (0·5 g), washed and defatted with ether, are added, and the mixture is boiled for 5 min. The liquid is decanted, the wool is washed in running water, and boiled again for 5 min. with water (100 ml) and dil. HCl (2 ml). The liquid is decanted and the treatment is repeated until the washings are colourless. After being washed thoroughly to remove the acid, the wool is boiled for 10 min. with water (50 ml) and aq. NH_3 (sp. gr. 0·910)

(10 drops), and the solution is diluted to 100 ml, boiled until all NH_3 is expelled and made distinctly acid to litmus with dil. HCl (2 ml); bleached wool fibres (0·06 g) are then added. The mixture is boiled for 5 min. and the wool is washed thoroughly in running water. A red (from red wine) or yellow (from white wine) coloration of the wool indicates the presence of an acidic organic dye. If the coloration is indistinct the treatment with aq. NH_3 and adsorption on the wool (0·03 g) should be repeated. The development of a rose colour during this second adsorption indicates the presence of an acid coal-tar dye. By comparison with the colours given by a series of standard solutions of Bordeaux red B, the approx. amount of dye in the wine can be estimated. Natural colouring matter does not interfere. S. C. JOLLY

473. **Comparison of different methods for the determination of aldehydes in brandy. I.** J. Lafon and P. Couillaud (*Ann. Falsif.*, 1954, **47**, 252–258).—The acidimetric method by reaction with NH_2OH requires large samples and is applicable only for an aldehyde content $>$ 0·01 per cent. A technique is described to minimise the errors. The iodimetric method (Jaulmes *et al.*, *Ann. Falsif.*, 1935, **28**, 325) is described and total aldehydes are estimated by this and the other methods. Apparatus, photometric and visual, and methods for the colorimetric determination of aldehydes with Schiff's reagent are discussed. E. J. H. BIRCH

474. **Comparison of different methods for the determination of aldehydes in brandy. II.** J. Lafon and P. Couillaud (*Ann. Falsif.*, 1954, **47**, 357–372).—Factors affecting colour development in a number of colorimetric methods for determining aldehydes (see preceding abstract) have been examined; a modified method is suggested, suitable for control analysis of brandy. *Procedure*—To 10 ml of distillate containing $>$ 0·14 g of aldehyde per litre, are added 2·5 ml of Schiff's reagent [30 ml of 0·1 per cent. fuchsin solution in aldehyde-free alcohol (95 per cent.) are added to 8 g of $K_2S_2O_5$ dissolved in 150 ml of double-distilled water, followed by 55 ml of 3 *N* H_2SO_4 and the mixture is diluted to 250 ml with double-distilled water]; the tube is stoppered and heated in a water-bath at 25° C for 20 min. The colour is measured in a suitable colorimeter; the amount of aldehyde present is derived from a standard curve, prepared from dilutions with aldehyde-free alcohol (50 per cent.) of a standard solution containing 0·20 g of acetaldehyde per litre. S. C. JOLLY

475. **Effect of antibiotics on organisms used in certain microbiological assays of essential nutrients.** G. G. Jackson, G. J. Gabuzda and M. Finland (*J. Lab. Clin. Med.*, 1954, **44** [3], 449–462).—The sensitivities of 10 test organisms to 9 antibiotics in the media used for amino-acid and vitamin microbiological assays are generally similar to those in conventional broth and agar media. In concn. up to 100 μg per ml in synthetic amino-acid medium at pH 7·4, the antibiotic activity of chlortetracycline (**I**) and oxytetracycline (**II**) is destroyed by autoclaving, but that of chloramphenicol (**III**) remains. **I**, **II** and **III** added to the medium (up to 100 μg per ml) before autoclaving, or added in sub-inhibitory concentrations to the autoclaved medium, could not replace any of 11 essential amino-acids in supporting the growth of appropriate test organisms. The activity of **I** against *L. casei* (7469) and *L. citrovorum* could not be counteracted by large concn. of riboflavine and citrovorum factor, respectively, whilst **I** added before autoclaving had no effect on the response of *L. casei* to graded sub-optimal amounts of riboflavine. **I** added to the appropriate autoclaved medium could not replace optimum amounts of nicotinic acid, riboflavine, citrovorum factor or pyridoxine. Partial folic acid activity of autoclaved **I** was traced to an impurity. W. H. C. SHAW

476. **Spectrophotometric determination of vitamin D in presence of vitamin A.** D. T. Ewing, T. D. Schlabach, M. J. Powell, J. W. Vaitkus and O. D. Bird (*Anal. Chem.*, 1954, **26** [9], 1406–1409).—A method for the determination of vitamin D in oil samples is given. The sample is saponified with alcoholic KOH and the non-saponifiable portion is extracted into ether. The extract is evaporated to dryness and the residue is taken up in hexane-ether soln. (5 + 1, by vol.). Chromatographic separation on an activated earth, Superfiltrol, is carried out to remove vitamin A, related carotenoids, pigments and some sterols; a second chromatographic separation on activated alumina removes certain polyenes as well as other compounds from the oil and Superfiltrol. The vitamin D is finally determined by measurement of its absorption max. at 265 mμ. Mean deviations between −12·9 and + 9·3 per cent. were attained over the range 2,980 to 44,000 U.S.P. units of vitamin D per g of oil, provided the vitamin A to vitamin D ratio was less than 10 to 1. The method was successfully applied to crystalline vitamin D_2 and vitamin-A acetate in maize oil, irradiated ergosterol and vitamin-A palmitate in maize oil, some fish-liver oils and miscellaneous samples. G. P. COOK

477. **Simple methods for the evaluation of microbiological assays of vitamins.** G. Marten (*Pharmazie*, 1954, **9** [6], 495–498).—Simple routine graphical methods are described for evaluating the results of microbiological assays. Calculations of variance are considered to be unnecessary for routine work. The assay of vitamin B_{12} (with *E. coli*) in liver extract and nicotinic acid (with *L. arabinosus*) are quoted as typical examples. P. S. STROSS

478. **Contribution to the determination of vitamin D.** J. Brüggemann, K. Blunk, W. Krauss and H. Karg (*Pharmazie*, 1954, **9** [6], 446–452).—In this short critical review of biological assays of vitamin D, preference is given to the X-ray method of Scheunert (*Vitamine und Hormone*, 1942, **3**, 37). It is considered more precise than other methods and the accuracy is claimed to be ± 10 per cent. in favourable cases, when groups containing as few as five rats, specially selected for uniformity of strain, size, etc., are used. The rats need not be sacrificed and the progress of the rickets can be followed from day to day. Time is saved as it is possible to construct calibration graphs, and permanent records that can be re-evaluated later are obtained. Enlargements of X-ray photographs of the proximal ends of the tibias of each test rat are made. The apparent separation (E) between the epiphysis and diaphysis, and the diameter (T) of the proximal diaphysis of each tibia are measured. A function of $\frac{E}{T}$ is plotted against vitamin-D dosage.

P. S. STROSS

479. **The determination of total tocopherol.** J. R. Edisbury, J. Gillow and R. J. Taylor (*Analyst*, 1954, **79**, 617–623).—A modified Emmerie and Engel test has been developed to avoid non-linearity, high or variable blanks and use of corrosive solvents. The sample is saponified in presence of gallic acid or pyrogallol, the unsaponifiable matter is extracted with ether, the solvent is removed in an inert atmosphere and the residue is dissolved in light petroleum. With samples containing < 40 μg of tocopherol per g, 10 to 20 g are extracted with ether in the presence of gallic acid or pyrogallol for 2 hr. in a Tait thimble, and, after removal of the solvent, saponification proceeds as before. The soln. of unsaponifiable matter is run through a chromatographic column of mildly alkaline alumina (prep. described) under slight air pressure, the adsorbed material is washed with an ether and light petroleum mixture and the tocopherol is subsequently eluted with $CHCl_3$. The eluate, which is concentrated by evaporation, is treated with soln. of $FeCl_3$ and 2:2′-dipyridyl in $CHCl_3$ and centrifuged with a measured amount of water; the optical density of the aq. soln. is determined at 520 mμ. The colour may also be measured visually, *e.g.*, by comparison with standard $CoSO_4$ soln. The only interference has been from highly oxidised carotenoids, for which a means of correction is given. The method was devised for determination of tocopherol in feeding stuffs, but it is applicable generally. A. O. Jones

480. **Microbiological determination of the B complex vitamins in horse-chestnuts and elderberries.** H. Haenel (*Pharmazie*, 1954, **9** [6], 489–495).—Horse-chestnut and elderberry extracts were examined for vitamin B_6 (pyridoxal, pyridoxamine and pyridoxine) with *Neurospora mutante sitophila*; for inositol, choline and thiamine with *Neurospora crassa*; for biotin, pantothenic acid and nicotinic acid with *Lactobacillus arabinosus*; for folic acid with *Streptococcus faecalis*; for vitamin B_{12} with *L. leichmanii*; for riboflavine with *L. casei*; for methionine with *Leuconostoc mesenteroides*; and for *p*-aminobenzoic acid with *Acetobacter suboxidans*. The methods used are described in detail. The amounts found in μg per g in horse-chestnuts and elderberry, respectively, were: vitamin B_6, 4·2 and 1·8; inositol, 2000 and 632; choline, 1080 and 95; thiamine, 1·2 and 1·1; biotin, 0·25 and 0·009; pantothenic acid, 9·3 and 2·4; folic acid, 0·23 and 0·1; vitamin B_{12}, 0·00007 and 0·00005; nicotinic acid, 106 and 6·6; riboflavine, 1·42 and 0·72; *p*-aminobenzoic acid, 0·2 and 0·5; and methionine, 1·400 μg per g (of horse-chestnuts). P. S. Stross

481. **The microbiological determination of vitamin B_{12} in complex organotherapeutic extracts.** J. Beck (*Ann. Pharm. Franç.*, 1954, **12** [2], 132–144).—The occurrence of accessory growth factors (accelerating or retarding) in liver extract containing vitamin B_{12} is discussed and the establishment of a suitable standard for microbiological assay is considered. A proposed method involves the growth effect on *Lactobacillus leichmanii* ATCC No. 7830/313 and the use, as standards, of (*i*) alkaline liver extract autoclaved to destroy vitamin B_{12} only and subsequently neutralised, and (*ii*) autoclaved acidic liver extract solution, which is subsequently neutralised, both vitamin B_{12} and peptide factors being destroyed, and to which is subsequently added a known amount of vitamin B_{12}. Details of technique and interpretation of results are given and it is found that a vitamin B_{12} soln. containing no peptones, peptides or amino-acids can be determined by using a mutant of *E. coli*. F. R. Mumford

482. **Colorimetric determination of ascorbic acid New developments concerning the reaction with diazotised 4-methoxy-2-nitroaniline.** M. Schmall, C. W. Pifer, E. G. Wollish, R. Duschinsky and H. Gainer (*Anal. Chem.*, 1954, **26** [9], 1521–1522).—The reaction between ascorbic acid and diazotised 4-methoxy-2-nitroaniline in acid medium, followed by the addition of alkali, yields an intensely blue colour. The final product has been identified as the deep-blue disodium salt of oxalic acid 4-methoxy-2-nitrophenylhydrazide. Analytical applications of this reaction have been developed and reported by Schmall, Pifer and Wollish (*Anal. Chem.*, 1953, **25**, 1486). Modifications of this procedure for the determination of ascorbic acid in milk and animal feed are described. G. P. Cook

See also Abstracts 369, 370, 504.

Sanitation

483. **Comparative studies of the dilution and Warburg methods for determining B.O.D.** E. W. Lee and W. J. Oswald (*Sewage Ind. Wastes*, 1954, **26** [9], 1097–1108).—Various aspects of the differences between the Warburg B.O.D. and the dilution B.O.D. tests have been compared. The advantages and disadvantages of these methods in respect of laboratory space required, cost of apparatus, technical skill, time and significance of results are compared. A. Webster

See also Abstracts 286, 313, 489, 490.

Agriculture and Plant Biochemistry

484. **Ultra-violet absorption spectra as a measure of phenolic hydroxyl group content in polyphenolic tannin-like materials.** L. F. Maranville and O. Goldschmid (*Anal. Chem.*, 1954, **26** [9], 1423–1427).—The method is based on the u.v. absorption of phenolic hydroxyl groups in alkaline soln. Measurement of a soln. at pH 10 is made directly against a soln. at pH 2·5 of the same sample. The absorption is measured over the range 260 to 360 mμ, 2 to 3-mμ intervals being taken near the two max. at $\simeq$ 290 and 330 mμ. Errors due to decomposition of the alkaline soln. are minimised by taking measurements of the phenol peak at three different times and extrapolating as a function of time from the instant of preparation of the alkaline soln. The method was compared with the purely chemical 2:4-dinitrophenyl ether method; the results were in close agreement. G. P. Cook

485. **Determination of phenolic hydroxyl content of lignin preparations by ultra-violet spectrophotometry.** O. Goldschmid (*Anal. Chem.*, 1954, **26** [9], 1421–1423).—The method is based on the u.v. absorption of phenols in alkaline soln. The absorbance of an alkaline soln. of lignin (pH 12) is measured directly against a nearly neutral portion (pH 6) of the same soln. The phenol content is calculated from the absorption max. of the resulting difference curve; the molar absorptivity max. of model phenols are determined in the same way. The max. are at approximately 250 and 300 mμ for simple substituted aromatic hydroyl compounds. The method is limited to non-conjugated phenolic hydroxyl groups. G. P. Cook

486. **The choice of a reagent for the classification of natural agricultural phosphates as a function of their fertilisation value.** P. Fleury (*Chim. et Ind.*, 1954, **72** [1], 59–66).—The methods of Wagner,

Robertson and Gingembre for determining the phosphate solubility, under approximately soil conditions, of various fertiliser minerals are reviewed. These methods are criticised because of carbonate interference and inadequate resolution of various rock types. It is recommended that phosphate minerals are evaluated by agitation with a 25 per cent. solution of Na citrate (pH 4·85) for 6 hr., followed by phosphate assay of the supernatant liquid by a standard method. Carbonate is partially dissolved under these conditions, and a classification of rock fertilisers by this method is in agreement with agricultural experience. The effect of grain-size upon phosphate solubility is studied for Constantine 65 and it is shown that variations of less than 140 μ have little effect. C. G. TAYLOR

487. **Determination of 2:4-dichlorophenoxyacetic acid, 2:4:5-trichlorophenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid and 4-chlorophenoxyacetic acid in technical mixtures by isotope-dilution analysis.** P. Sorensen (*Anal. Chem.*, 1954, **26** [10], 1581–1586).—Radioactive 2:4-dichlorophenoxyacetic acid (**I**), 2:4:5-trichlorophenoxyacetic acid (**II**), 4-chloro-2-methylphenoxyacetic acid (**III**) and 4-chlorophenoxyacetic acid (**IV**) were prepared from radioactive ^{36}Cl and these were used for the isotope-dilution procedures described. Methods for the determination of **I** alone, **I** and **II** together, **II** alone, **III** alone and **IV** alone are given. The percentage standard deviation for the determinations is within $\pm$ 1 per cent. The methods were applied successfully to the analysis of technical samples and agricultural preparations.

G. P. COOK

488. **Isolation of pentachloronaphthalene from cotton-seed feed pellets.** R. T. Blickenstaff and J. E. Callen (*Anal. Chem.*, 1954, **26** [10], 1586–1589).—Pentachloronaphthalene (**I**) was isolated from cotton-seed pellets by the following procedure. Finely ground pellets were extracted with ether in a Soxhlet extractor, the ether soln. was evaporated and the liquid residue was saponified by heating under reflux with ethanolic KOH. The hydrolysate was then extracted with light petroleum and the extract was evaporated to constant wt. The unsaponified fraction was then dissolved in light petroleum and chromatographed on a column of alumina. Fractions containing Cl were extracted with a methanol - 2:2:4-trimethylpentane mixture, and the combined residues were crystallised from ethanol. The material isolated gave i.r. and u.v. spectra, X-ray diffraction patterns and m.p. in agreement with authentic **I**. As little as 8 p.p.m. of **I** can be isolated from cotton-seed feed pellets by this procedure. G. P. COOK

489. **Paper chromatography of the systemic insecticides Demeton and Schradan.** R. B. March, R. L. Metcalf and T. R. Fukuto (*J. Agric. Food Chem.*, 1954, **2** [14], 732–735).—Chromatography on silicone-impregnated filter-paper separates OO-diethyl O-2-ethylthioethyl thionophosphate (Demeton) from its thiol isomer, OO-diethyl S-2-ethylthioethyl thiophosphate, and their main plant metabolites. The upper phase of the system chloroform - ethanol - water (10:10:6, by vol.) is used as solvent. In an alternative technique, the paper is impregnated with propylene glycol and the solvent is a mixture of petrol and toluene (4:1 by vol.) saturated with propylene glycol. Octamethylpyrophosphoramide (Schradan) and related phosphoramide esters are chromatographed on paper treated with propylene glycol by use of equal volumes of benzotrichloride, CCl_4 and toluene, saturated with propylene glycol as solvent; the concn. of the glycol is critical. R_F values for the insecticides and related compounds are recorded. Schradan is revealed on the chromatogram by spraying with a mixture of 72 per cent. $HClO_4$, 4 per cent. ammonium molybdate, *N* HCl and water (5:25:10:60, by vol.), heating at 80° C for 2 min. and exposing to u.v. light (365 mμ) for 15 to 30 min. The more easily hydrolysed compounds give blue spots in a short time, the others within 24 hr. Not all the spots have been definitely identified. The technique is less satisfactory for Demeton as the colours take 24 to 72 hr. to develop, but if the compound is labelled with ^{32}P or ^{35}S, location by counting along the strip or by autoradiography is good. The anticholinesterase activity of segments of the chromatogram can also be estimated manometrically. C. E. SEARLE

490. **The separation of contact insecticides (DDT, E605, BHC) by paper chromatography.** W. Gruch (*Naturwissenschaften*, 1954, **41** [2], 39).—The test material is dissolved in acetone and applied to Schleicher and Schüll paper No. 2043b impregnated with diethyl ether containing 2 per cent. of Vaseline. The developing solvent consists of ethanol (96 per cent.), water and aq. NH_3 soln. (sp. gr. 0·91) (80:15:5). An ascending technique is used. The strips are cut into segments and each segment is eluted with water and tested for insecticide by the addition of larvae of *Aedes aegypti* to the eluate. From the position of the lethal max. concn. of the insecticide its R_F value was calculated; the value for DDT is 0·63, BHC (hexachloro*cyclo*hexane) 0·87 and E605 (parathion) 0·95. Samples containing E605 also show a characteristic yellow band with an R_F value of 0·80 caused by free nitrophenol. The band is clearly visible on the wet strip and can be revealed on the dry strip in u.v. light.

E. KAWERAU

See also Abstracts 306, 307, 321.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

491. **Compressed glass-to-metal seals.** H. Adam (*J. Soc. Glass Tech.*, 1954, **38**, T 285–T 296).—The stresses in a "window seal" of a glass disc within a metal tube, with and without a central rod(s) through the glass, are analysed theoretically. Examples are given of seals between a mild steel tube of 1¼-in. bore and a mild steel rod of 1⅛-in. diameter, and of a mercury-pool cathode assembly with an inner steel cone of 3-in. diameter. The advantages of mild steel are cheapness, good electrical conductivity and ease of machining, cleaning and joining to other metals.

J. A. SUGDEN

492. **Metal-to-glass seals for vacuum work at low temperatures.** J. E. Quarrington (*J. Sci. Instrum.*, 1954, **31** [10], 387–388).—A thin (0·2 mm) copper corrugated disc may be sealed to Pyrex-glass tubing (2·8 cm diam.) by Araldite cement.

G. SKIRROW

493. **Glass plate heater for paper chromatography.** W. R. Fetzer and L. D. Ough (*Anal. Chem.*, 1954, **26** [10], 1671).—A glass plate heater is used instead of an oven for heating paper chromatograms after treatment with detecting agents. Direct contact between paper and heater is avoided by interposing

a stainless-steel screen of 0·25-in. mesh, and a rotary motion is imparted to the chromatogram. The method has the great advantage of permitting visual inspection during the whole operation.
J. H. WATON

494. **Devices for gradient elution in chromatography.** R. M. Bock and Nan-Sing Ling (*Anal. Chem.*, 1954, **26** [10], 1543–1546).—The theory underlying a composition controller for eluents is considered; it is applied to systems consisting in a cylinder containing a radially symmetrical vessel. If the concn. of the eluent is to vary as some arbitrary function, $C = C_1 + f(v)$, of the vol. of eluent delivered, then an inner vessel can be constructed whose radius varies according to the relation $kr^2 = f(v)$. Other devices are described that allow a general soln. of $C = f(v)$. These devices should prove of use in ion exchange or column chromatography, or in other processes in which a soln. of gradually changing concn. is required. J. H. WATON

495. **Gas flow counter for scanning paper chromatograms and paper ionograms.** H. L. Demorest and R. Baskin (*Anal. Chem.*, 1954, **26** [9], 1531–1532).—An apparatus suitable for counting β-particles from compounds tagged with ^{14}C is constructed out of a gas flow counter. The chromatogram is drawn automatically along the main chamber, which is separated by a slotted plate from the counting chamber above. After passing through the slit, the β-particles are detected in the counting chamber, which is fitted with a tungsten-wire anode. The sensitivity of the instrument gives a counting rate of twice the background for $0{\cdot}15 \times 10^{-3}$ mC of ^{14}C, but with an actual chromatogram the sensitivity may be only a tenth of this value. J. H. WATON

496. **Calculator for use with fluorescent indicator adsorption method.** W. H. Ellis (*Anal. Chem.*, 1954, **26** [10], 1672).—A proportional divider of the right-trapezoid type, 50 and 80 cm in length and 48 cm in height, is constructed on paper and divided into 100 equal divisions. The chart is mounted on a Lucite cylinder 6 in. in diameter, into which is fitted a fluorescent light. The chromatographic column, marked under u.v. light, is laid in a glass trough and placed over the cylinder. The lower mark on the column is put over the 0 per cent. line and the cylinder is rotated until the upper mark intersects the 100 per cent. line. The percentage of each zone on the column can then be read directly. J. H. WATON

497. **Apparatus for automatically scanning two-dimensional paper chromatograms for radioactivity.** W. J. Wingo (*Anal. Chem.*, 1954, **26** [9], 1527–1528).—An apparatus is described for scanning a two-dimensional chromatogram along a helical path. The radiograph of the chromatogram results traced out can furnish roughly quantitative results.
J. H. WATON

498. **A new laboratory extraction apparatus: the B.B.S.** M. Saulnier (*Ann. Falsif.*, 1954, **47**, 249–251).—An extraction apparatus is described in which the reflux condenser is in two parts: a lower part with an external water-jacket, carrying a tap at its lower end and by-passed with a side tube, and an upper part with an internal cooling tube through which ice-water may be passed without external condensation. The solvent refluxes on to the material contained in an extraction tube with a sintered-glass base and back to a flask weighing 60 to 100 g, so that after removal of the solvent by closing the tap and collecting it in the lower condenser, the flask and extracted matter may be directly weighed. E. J. H. BIRCH

499. **Modification of the Schmall extractor.** M. Schmall, C. W. Pifer and E. G. Wollish (*Anal. Chem.*, 1954, **26** [10], 1670).—The previously described Schmall extractor for solvents lighter than water (*Brit. Abstr. C*, 1953, 11) has been modified. The lower side-arm and the baffle plate are eliminated and the solvent enters the flask at the centre of the vortex instead of at the side. The flask can readily be connected to a reflux condenser for hydrolysis or saponification reactions.
J. H. WATON

500. **All-glass automatic water-distillation apparatus.** F. Highhouse, C. Mencken and J. B. Moloney (*Rev. Sci. Instrum.*, 1954, **25** [10], 1038–1039).—An apparatus is described for the provision of thrice-distilled water. After pre-heating to eliminate volatile gases, the water is admitted to the first of three distillation flasks arranged in cascade. The water level in the first flask is controlled by a constant-head device. Micro switches actuated by floats in the second and third flasks switch off the heating current when the water level is too low. G. SKIRROW

501. **Automatic syphon fractionator. Design and characteristics of syphons for polar and non-polar liquids.** J. Bové (*Anal. Chim. Acta*, 1954, **11** [5], 431–437).—Syphons used in chromatographic fractionations are required to deliver fractions of constant volume. Principles of design have been determined for the attainment of the greatest constancy with liquids of diverse physical characteristics. When an automatic turn-table is used for the receivers, the syphon regulates the electrical impulses that operate the table. A float-operated contact is described for use with non-conducting liquids. W. C. JOHNSON

502. **Efficient laboratory freeze-drying apparatus.** A. L. Tappel (*Anal. Chem.*, 1954, **26** [10], 1671–1672).—A freeze-drying apparatus is described which can be made from generally available laboratory equipment. It is convenient in use as the sample is visible, the sample temp. and total pressure are measured and only one vacuum seal is broken in opening the freeze-dryer vacuum chamber. With the apparatus, a 1-in. thick beefsteak can be freeze-dried to 10 per cent. moisture in approx. 24 hr. J. H. WATON

503. **A ball and cup absolute microviscometer.** P. D. Garn and W. E. Campbell (*Anal. Chem.*, 1954, **26** [10], 1609–1613).—The ball and cup viscometer is shown to give reasonably accurate values for absolute viscosity on samples as small as 0·035 ml. The viscosity range covered by the inversion technique can be extended to lower viscosities if the balance technique, in which a variable force is applied to lift the ball from the cup, is used. The drop time of the first technique and the pull-up time of the second are related to the absolute viscosity by the equation $\eta + kt + c$, c being a small correction determined by calibration. The method is quick, requires very small amounts of sample, which are recoverable, and gives values showing a standard deviation usually < 2 per cent.
J. H. WATON

504. **A new apparatus for wet mineralisation.** J. Pien (*Ann. Falsif.*, 1954, **47**, 266–272).—The disadvantages of the classical method of mineralisation with acids in an open flask are discussed, and an apparatus is described in which volatile substances are recovered and returned to the flask; speed is increased by avoiding the necessity of cooling between additions of reagent and liberation of volatile acids into the atmosphere is avoided. A flask of the required size is attached by a standard spherical joint to a tube leading to the top of a receiver for the distillate, at the bottom of which is a tap through which the contents may be returned to the flask. A tap funnel is also provided for the addition of reagent. A reflux condenser, connected at its top to a water-pump, fits on to the top of the receiver. For a mineralisation with H_2SO_4 - HNO_3, the sample (5 to 100 g) is covered with 50 ml of HNO_3 (sp. gr. 1·33) and 20 ml of H_2SO_4 (sp.gr. 1·84) are added. The flask is heated, HNO_3 is put into the tap funnel and added in small amounts as soon as a brown colour is seen in the liquid. When the primary mineralisation is complete, the tap of the reflux receiver is opened and the mineralisation of its contents completed in the flask if necessary. Any distilled fatty acids collect on the top and need not be returned to the flask. A comparison with the open flask method is given for several materials; a great saving of time and of nitric acid is claimed. E. J. H. BIRCH

505. **Micro-balance without a beam rider.** O. Pfundt (*Mikrochim. Acta*, 1954, [5], 539–544).—The construction of a riderless micro-balance is described. Two models have been made, one for max. loads of 20 g and the other for 10 g. Fractional weights from 1 mg are added by a mechanical device and there is a projection scale for 0 to 1 mg. The beam of the balance is enclosed in a separate compartment. The left-hand pan can be removed, for the addition of small objects for weighing, without the necessity of opening a panel in the case. The 10-g model has an automatic tare device, a separate rider for testing sensitivity and an arrangement for regulating the sensitivity from outside. A. J. MEE

506. **Simple automatic measure.** S. Graham (*Lab. Practice*, 1954, **3** [11], 460).—A bank of automatic filling pipettes is connected to a common supply line from an aspirator. Flow, to and from the pipettes, is controlled by the rotation of eccentrically mounted metal rods; these can press rubber-tubing extensions of the inlet and outlet tubes against a fixed metal bar. G. SKIRROW

507. **Two improved control systems for horizontal micro-burettes.** A. G. Hamlin and J. M. Bather (*Analyst*, 1954, **79**, 655–657).—Two control systems of horizontal micro-burettes are described and illustrated. They combine reasonably rapid delivery with adequate control near the end-point of a titration. The first assembly permits very accurate control, but it must be possible to complete the titration within the capacity of the plunger of the fine control valve, which must be reset before each titration. In the slightly less-precise second assembly, this disadvantage is overcome. In both forms, most of the titration is effected by manipulation of one valve, but as the end-point is approached the titration is completed by manipulation of a second finer valve. A mercury trap enables the burettes to be filled and cleaned rapidly.
A. O. JONES

508. **Laboratory pump for closed circulation of humidified air.** C. Wood (*J. Sci. Instrum.*, 1954, **31** [10], 386–387).—The double-acting pump described is constructed from a pair of rubber bellows jointly actuated by a motor and reduction gear in such a way that one is compressed when the other is expanded. Each bellows carries an inlet and an outlet valve. The pump circulates 2 cu. ft. of air per min. against a pressure head of 10 in. of water. G. SKIRROW

See also Abstracts 285, 414, 467.

Optical

509. **Electrodes for spectrochemical analysis.** A. Rodríguez Pérez (*Inf. Quím. Anal.*, 1954, **8** [5], 157–163).—The advantages of copper as opposed to carbon electrodes are pointed out.
L. A. O'NEILL

510. **Insert for reducing volumes of Beckman spectrophotometer.** L. H. Sharpe (*Anal. Chem.*, 1954, **26** [9], 1528).—An insert constructed from Teflon to fit into a Beckman 1-cm cell reduces the vol. of solution required from 3 to 1 ml without reducing the length of the light path, and yet permits complete passage of the light beam from the monochromator. J. H. WATON

511. **Simple high-temperature microwave spectrograph.** P. A. Tate and M. W. P. Strandberg (*Rev. Sci. Instrum.*, 1954, **25** [10], 956–958).—A stainless-steel wave guide equipped with a Stark septum and enclosed in a vacuum-tight envelope is used as a microwave absorption cell for studies in the temperature range 600° to 1000° C. Details are given of the furnace and temperature-control equipment used. G. SKIRROW

512. **Use and characteristics of photocolorimeters.** F. Braun (*Chim. Peint.*, 1954, **17** [4], 110–119).—The characteristic features of photocolorimeters are described. Values obtained for three-colour co-ordinates on a number of colorimeters are compared with those given by the Hardy spectrophotometer. L. A. O'NEILL

513. **Nephelometer of wide range for bacteriological use.** E. O. Powell (*J. Sci. Instrum.*, 1954, **31** [10], 360–362).—Light from a slit is brought to a focus after passing through a suspension. The direct (transmitted) light is compared with that scattered. The intrument behaves as a nephelometer at low concentrations and like an absorptiometer at high ones, and will cover a range of 10^6 organisms per cu. cm to more than 10^{10} per ml. The design and constructional details are given.
G. SKIRROW

514. **A twin-beam null-point fluorimeter for the analysis of liquid samples.** J. P. Dowdall and H. Stretch (*Analyst*, 1954, **79**, 651–655).—A twin-beam fluorimeter is described and illustrated. The source of light is a 12-V 24-W tungsten lamp. The detector system consists of two photo-multipliers, one on each side of the lamp, connected together with the final dynode load resistors, one of which is variable, in a bridge circuit; a galvanometer is joined between the final dynodes. The test cells are of glass. Power comes from a constant-voltage transformer supplying a lamp transformer at 12 V and 2 to 3 amp. and a stabilised 1000-V, 2 to 3-mA supply. The power supply to the photo-multipliers is controlled by a potentiometer. The instrument is normally used at 900 V. The galvanometer is set to a null point with a fluorescent soln. of known

strength; the soln. is replaced by the test soln. and the potentiometer is adjusted until the galvanometer again indicates the null point. The potentiometer reading corresponds to the fluorescent value of the test soln. The reading, corrected for a reagent blank, is referred to a calibration graph prepared with known wt. of the test substance. With appropriate filters, 0·01 μg of riboflavine and Na naphthionate in 2 ml of soln. can be determined, and 0·001 μg of fluorescein can be measured, the assumption being made that these bodies are stable at these dilutions. A. O. JONES

See also Abstract 289.

Thermal

515. **Remotely controlled surface evaporator for routine analytical work.** E. H. Turk and L. S. Markheim (*Anal. Chem.*, 1954, **26** [10], 1668–1669).—A rack containing up to four centrifuge tubes is raised slowly, so that the tubes pass through narrow coil heaters at approx. the rate of evaporation of the soln. After a pause to ensure complete dryness at the bottom of the tubes, the rack is lowered to remove any condensate on the upper portion of the tube. J. H. WATON

516. **Analytical procedures using a combined combustion - diffusion vessel. Improved method for combustion of organic compounds in aqueous solution.** J. Katz, S. Abraham and N. Baker (*Anal. Chem.*, 1954, **26** [9], 1503–1504).—A combined combustion - diffusion apparatus, by means of which persulphate oxidation of water-soluble organic compounds is greatly simplified, is described. The CO_2 evolved in the combustion is collected in NaOH soln. and is determined by titration of the carbonate formed with standard acid. Of eighteen organic compounds determined by this method, 17 gave recoveries between 96 and 102 per cent. and one of 80 per cent. The method was used principally by the authors for ^{14}C determination. G. P. COOK

517. **Analytical procedures using a combined combustion - diffusion vessel. Simple wet-combustion method suitable for routine carbon-14 analyses.** N. Baker, H. Feinberg and R. Hill (*Anal. Chem.*, 1954, **26** [9], 1504–1506).—The apparatus consists of a screw-capped bottle containing a smaller compartment within. A mixture of sample and van Slyke - Folch combustion mixture (*J. Biol. Chem.*, 1940, **136**, 509) is placed in the bottle and CO_2-free NaOH is placed in the inner compartment. The apparatus is heated in an autoclave or pressure-cooker, cooled and the Na_2CO_3 - NaOH is dissolved in water. Barium chloride is added to this soln. and the excess of base is determined by titration with standard acid. A ^{14}C-fatty acid yielded 98 to 105 per cent. recoveries; ^{14}C-glucose and ^{14}C-phenylglucosazone recoveries were 95 to 104 per cent. and 91 to 100 per cent., respectively. G. P. COOK

518. **Temperature control of a large water-bath using a resistance thermometer.** W. P. Hutchinson, E. W. Pulsford and A. G. White (*J. Sci. Instrum.*, 1954, **31** [11], 420–424).—Apparatus is described for providing temp. control within ± 0·001° C for a 500-litre water-bath. G. SKIRROW

519. **A new melting-point apparatus.** G. Westerburg (*Dtsch. ApothZtg.*, 1954, **94** [24], 544–545).—A new melting-point apparatus (of modified Thiele type), also applicable for sublimation and boiling-points, is described. F. R. MUMFORD

Electrical

520. **Control to protect against damage by interruption of cooling water flow.** D. H. Anderson and R. G. Smith (*Anal. Chem.*, 1954, **26** [10], 1669).—A flow switch is described which is fitted in the outlet line of a cooling system; it operates only when water is actually flowing. In rising vertically through an orifice, the water strikes a brass contact, operating a relay, which closes the power-supply circuit to the apparatus being heated. J. H. WATON

521. **Thermal circuit breaker for water-cooled systems.** S. Soloway and F. J. Rennie (*Anal. Chem.*, 1954, **26** [10], 1669–1670).—Water from a cooling system is passed through a brass chamber, which is surrounded by a heating coil. Inside the chamber is a thermoswitch, which can be set to open at any desired temp. to shut off the power supply to the whole apparatus. The thermoswitch will operate when the temp. of the water in the chamber rises above the pre-set value, either because the temp. of the water from the cooler has risen or because the flow has ceased. J. H. WATON

522. **General review of polarography.** W. van Tongeren (*Chem. Weekbl.*, 1954, **50** [45], 769–777).—This introductory paper to a symposium on polarography (see Abstracts, 366, 385 and 406) deals with the general theory of polarography and the place of the method in electrochemical analysis. The factors affecting the magnitude of the diffusion current are considered, and the instruments used in polarography are described. A. J. MEE

523. **Polarography with a dropping-gallium electrode.** P. A. Giguère and D. Lamontagne (*Science*, 1954, **120**, 390–391).—Although Ga liquefies above 29·7° C and might therefore serve as a dropping electrode, its other properties make it entirely unsuited to the purpose; this has been confirmed experimentally. Characteristics of a dropping-gallium electrode are recorded, but in view of its erratic behaviour no attempt was made to study reduction of other metal ions. H. F. W. KIRKPATRICK

524. **Improved trigger circuit for automatic titrations.** W. N. Carson, jun. (*Anal. Chem.*, 1954, **26** [10], 1673–1674).—Modifications have been made to improve the trigger circuit for automatic coulometric titrations previously described (*Brit. Abstr. C*, 1953, 330). The dry cell is replaced by an electronic equivalent, giving a constant voltage and stabilising the trigger setting. A delay action to the trigger is fitted to prevent oscillation of the auto-titrator or chatter at the end-points. J. H. WATON

525. **An automatic coulometric titrimeter.** N. Bett, W. Nock and G. Morris (*Analyst*, 1954, **79**, 607–616).—Coulometric titrimetry in which the titrant is generated externally is investigated by manual methods; the experimental error is shown to be ≃ 0·1 per cent. for titrations of 25 ml of 0·01 *N* acid or alkali. A modified form of electrolysis cell and a specially stabilised current supply are devised for titration of 0·1 *N* soln. Coulometric analysis, depending upon the flow of an electric current, is particularly suitable for automatic operation, and the construction of an automatic titrimeter incorporating an integrator capable of recording a quantity of electricity is described in detail.

Titrations of $Na_2S_2O_3$ by coulometrically generated I are described and the results are shown to be satisfactory. A. O. JONES

526. **Coulometric titrations. Automatic titrator for mercaptans.** F. A. Leisey (*Anal. Chem.*, 1954, **26** [10], 1607–1609).—An automatic titrator for determining mercaptans in petroleum stocks is described. The mercaptan is pptd. as silver mercaptide by Ag generated coulometrically, whilst the end-point is detected amperometrically. *Procedure*—A 1-ml sample of a solution consisting of 100 ml of 95 per cent. ethanol, 50 ml of benzene, approx. 0·5 g of NH_4NO_3 and 2 ml of aq. NH_3 soln. is used as an electrolyte. At the end-point, the amperometric circuit operates a relay that switches off the current and the electrical timer. For a given sample vol., the coulometric circuit may be adjusted so that the timer gives direct readings of mercaptan content. Samples containing as little as 2 μg can be titrated, and the agreement with potentiometric results is better than 2 per cent. for $\simeq$ 100-μg amounts. The coulometric current and sample vol. can be selected so that the titration time is from 2 to 5 min. The presence of CN', I', S'', S_2O_3'' and any other ions removing Ag from ammoniacal soln. interfere. J. H. WATON

527. **The mass spectrometer as an analytical instrument.** G. P. Barnard (*Analyst*, 1954, **79**, 594–607).—A brief description with illustrations of some modern instruments, operational techniques and analytical procedures is given. Indications of the wide range of work to which the mass spectrometer can be applied are given (*e.g.*, determination of hydrocarbons, alcohols, ethers, esters, trace elements and impurities). Its application to the analysis of stainless steels is also described. Mass spectrometry is shown to compare favourably with other physical methods of analysis. A. O. JONES

528. **Analytical mass spectrometry utilising relative abundance ratios.** J. B. Freeman and E. J. Serfass (*Anal. Chem.*, 1954, **26** [9], 1403–1405).—A conventional mass spectrograph is modified so that two widely separated masses, which are individually characteristic of the components of a binary mixture, produce a modulated beam of positive ions, which can be focused on a single exit slit. The ions are detected as a modulated ion current, and then separated by a de-modulator into the two ion currents, which are fed via filter networks into a ratio-measuring circuit. The analysis of the mixture is achieved by measuring the relative abundance ratios of the ion currents, measurements are accurate within $\pm$ 1 per cent. The method is independent of the sample pressure, of fluctuation in the instrument sensitivity and electron current. The evaluation from graphs drawn for known mixtures of the same components is rapid. J. H. WATON

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
critical	crit.
crystalline	cryst.
crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment	expt.
foot, feet	ft.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
maxim -um, -a	max.
melting-point	m.p.
mitro-curie	μC
microgram	μg
micro-litre	μl
micron	μ
milliampere	mA
milli-curie	mC
milligram	mg
millilitre	ml
millimetre	mm
millimicron	mμ
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
ounce	oz
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. v/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	$n\lambda'$
relative humidity	R.H.
revolutions per minute	r.p.m
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]\lambda'$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

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CONTENTS

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